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Determination of Free Bromine in Water (U)

ANNUAL PROGRESS REPORT

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T. E. Larson and F. W. Sollo, Jr.

August 1967
(For the period 15 March 1966 to 30 June 1967)

U. S. Army Medical Research and Development Command

Washington, D. C. 20315

Annual Report to the Commission on Environmental Hygiene
of the Armed Forces Epidemiological Board

Contract No. DA-49-193-MD-2909

Illinois State Water Survey

Urbana, Illinois 61801

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I. SUMMARY

Twenty-seven colorimetric reagents were evaluated on the basis of their reactions with bromine, chlorine, chloramines and bromamines. At the present time methyl orange and phenol red are the best available reagents for total bromine, and are in good agreement. Brom cresol purple is the best available reagent for free bromine. Phenosafranin gives reasonably good results for free bromine, but its primary application may be in determining high concentrations of bromine (up to 10 mg/l).

Breakpoint curves with bromine and ammonia have been determined for varied contact times and at different pH values.

The bromamines are far less stable than the chloramines. Studies of the stability under varying ammonia-to-bromine ratios and varying pH values have been made.

A study was made of the reaction of chloramines with bromide ion. No evidence of bromamine formation was found by ultra-violet absorption, but stability of the chloramine solution was decreased, and it appears that unstable bromamine was formed slowly. The chloramine-bromide ion solutions exhibited characteristics similar to those of bromamine solutions. As with bromamine solutions, the stability of chloramine-bromide solutions may be improved by increasing the ammonia-bromine (or bromide ion) ratio or by increasing pH.

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V. DETERMINATION OF FREE BROMINE IN WATER

A. INTRODUCTION

Under certain circumstances neither chlorine nor iodine is entirely satisfactory as a viricidal and germicidal agent in the preparation of potable water. In the presence of ammonia, chlorine reacts to form chloramines which are far less effective than free chlorine; and iodine effectiveness decreases with decreasing pH and with increasing concentration of iodide ion. It was felt that bromine might possibly have properties which would avoid these problems, but greater knowledge of the chemistry of bromine and bromamines in dilute solutions is necessary for a thorough evaluation. If bromine were to be used as a germicidal agent, a suitable field method for its determination would be necessary. A suitable laboratory method would also be required for a thorough evaluation of the effectiveness of bromine as a viricide and germicide.

Monobromamine is reported to be a more effective bactericide than monochloramine. If waters of high ammonia content could be disinfected by the addition of bromine in small quantities to produce bromamine, the need for the use of chlorine in concentrations sufficient to produce free chlorine would be obviated. Bromamines can be formed by the addition of liquid bromine to water containing ammonia, or by the sequential addition of bromide ion and chlorine to waters containing ammonia. In the latter method, which would probably be preferred for field use, both chloramines and bromamines are formed. However, it appears that as bromamine is destroyed, the equilibrium shifts to produce more bromamine. If sodium bromide is added to water containing chloramine, the chloramine becomes less stable, probably due to the formation of bromamine, and will react with reducing agents not otherwise affected.

It is the purpose of this project to evaluate possible methods for the determination of bromine and bromamines in water, and the effect of possible interferences such as chlorine, chloramine, iron, nitrite, and manganese. Colorimetric tests have been given the greatest attention since they are more easily adapted for field use.

Twenty-seven reagents for bromine have been considered. Of these, 15 have been rejected as unsuitable, and 8 are not under serious consideration at present although they

still have potential value. The following 4 reagents were selected for detailed investigation:

1. Methyl orange
2. Phenol red
3. Brom cresol purple
4. Phenosafranin

These reagents were selected primarily because interferences due to chloramine, ferric ion, nitrite ion, and manganese are low. Methyl orange can be used as a quantitative reagent for total residual bromine and free chlorine; phenol red is a unique test for total bromine; brom cresol purple is nearly specific for free bromine with interference only from free chlorine; and phenosafranin may be useful in measuring high concentrations of free bromine and chlorine (up to 10 mg/l as Br_2). Free bromine calibration curves have been prepared for each reagent at temperatures of 2°, 10°, 20°, 30°, and 40°C. Phenosafranin and phenol red show no temperature dependence, while brom cresol purple and methyl orange show slight temperature dependence.

The work with each of these methods has been covered in the individual sections of this report.

B. EVALUATION OF FREE BROMINE TESTS

A number of reagents have been considered as possible colorimetric tests for free bromine. Included among these are the reagents earlier evaluated as chlorine tests.[1] Others were chosen from those suggested in the literature and those with low ORP values which, it was hoped, would permit oxidation by free bromine but not by free chlorine.

Many of these reagents proved to be unsatisfactory and have been discarded. These reagents are listed in Table 1 with the reasons for their elimination.

Other reagents, which would be satisfactory except for certain interferences, have been set aside in favor of a few reagents showing greater promise. Calibration curves may be prepared for all reagents of this class. Each reagent either was subject to chloramine interference or was similar but inferior to some other test under consideration. However, some sort of bromine test might be established for any one of these reagents. These are included in Table 2, which shows free chlorine, chloramine, or bronamine interference.

The four reagents, methyl orange, phenol red, brom cresol purple, and phenosafranin are under further study at the present time. None of these reagents is free of interferences, but each serves a particular purpose, and a combination of the tests may be used to determine both the quantity and form of the total residual halogen present. These reagents are discussed individually in the following portion of this report.

1. Methyl Orange (MO)

The colorimetric procedure[2] developed in this laboratory as a test for chlorine in water was evaluated for use with bromine. At this time the methyl orange test is being used to determine total residual bromine in waters containing no chlorine and to determine total residual bromine plus free chlorine if present. Addition of an excess of bromide ion to the sample allows determination of total residual bromine and chlorine.

Calibration curves for free bromine in water at temperatures 2°, 10°, 20°, 30°, and 40°C have been prepared (figure 1). The curves are linear and cover the range 0.0-4.0 mg/l of bromine. As for chlorine, the methyl orange test is

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1. T. E. Larson, F. W. Sollo, "Determination of Free Chlorine Residuals in Water", Final Technical Report to the Commission on Environmental Hygiene of the Armed Forces Epidemiological Board, Contract No. DA-49-193-MD-2399, 15 February 1963 to 31 August 1965.
2. T. E. Larson, F. W. Sollo; "Determination of Free Chlorine Residuals in Water", Final Technical Report.

TABLE 1

TESTS CONSIDERED UNSATISFACTORY AFTER PRELIMINARY SCREENING

Basis for Rejection of Bromine Tests:

Check (✓) indicates basis for rejection
Dash (-) indicates no data available

Test	Does not conform to Beer's Law	Not sensitive to Br_2	Free Cl_2 interference	Chloramine interference	Bromamine interference	Reagent not stable in solution	Test Color not stable	Other interferences	Comments
Benzidine	✓	-	✓	✓	-	-	-	-	
Bromphenol Blue	-	✓	-	-	-	-	-	-	
Chlorphenol Red		✓		-	-	-	-	-	
Cresol Red	✓		✓	-	-	-	-	-	
Diphenylbenzidine	-	-	-	-	-	✓	✓	-	Reagent highly unstable. Good less than one day. Test color not stable long enough to make determination.
Evans Blue & Trypan Blue	✓		✓		✓		✓		Both reagents demonstrate shifting wave lengths in direction of the violet range (560-570 mμ)
Ferroin	-	✓	-	-	-	-	✓	-	
Leuco Crystal Violet	✓		✓	✓	✓		✓		
Methyl Red			✓	✓	✓			Mn^{+3}	Rejected earlier on Cl_2 test. Similar to methyl orange but not as good.
N,N-dimethyl-p-phenylene-diamine			✓	✓	✓			Mn^{+3}	Rejected earlier on test for free Cl_2. Similar to DPD oxalate but not as good.
Neutral Red			✓	✓	✓			Mn^{+3}	Rejected earlier on Cl_2 test.
Sulfanilic acid-pyridine	-		✓	✓	✓	-	✓	-	Slow reaction time (6 min) Test not reproducible
Tetrakis				✓	-			NO_2^-	Rejected earlier on Cl_2 test.
Thymol Blue	✓		-	-	-	-	-	-	

TABLE 2

REAGENTS NOT UNDER CONSIDERATION AT PRESENT

A check mark indicates interference

Reagent	Interference		
	free Cl_2	chloramine	bromamine
DPD oxalate	✓	✓	✓
Acid OT	✓	✓	✓
Brom Cresol Green	✓	✓	✓
Brom Thymol Blue	✓	✓	✓
Indigotetrasulfonic acid	✓		✓
Methylene Blue	✓		✓
Neutral OT	✓		✓
Nile Blue A	✓		✓

slightly temperature dependent. Ferric and nitrite ions do not interfere, and the interference due to manganic ion may be eliminated by use of an arsenite modification of the methyl orange test. The rate of reaction of chloramine with methyl orange is shown in figure 2 and the extent of interference depends upon the time allowed before reading, normally 1.5 minutes. The presence of bromide ion in the sample promotes the chloramine reaction as shown in figure 3.

Reagents:

(1) 0.005% methyl orange diluted from a 0.05% solution, with 0.8242 g sodium chloride added per 500 ml of final solution.
(2) 91% chloroacetic acid
(3) 2.6% sodium bromide

Procedure:

To determine total residual bromine plus free chlorine, a 50 ml sample is added to 5 ml 0.005% MO containing 1 ml chloroacetic acid solution; this is mixed and absorbance determined 1.0-1.5 minutes after preparation at 510 mμ, pH 1.9. If the absorbance is less than 0.10, the test is re-run using 10 ml 0.005% methyl orange.

To determine total residual bromine and chlorine, 0.5 ml of 2.6% sodium bromide solution is added to the sample after the first determination has been completed. The solution is mixed and after 10 minutes the absorbance is again determined. If absorbance is less than 0.10, a new sample should be prepared using a larger quantity of methyl orange.

2. Phenol Red (PR)

An adaptation of the procedure described in Standard Methods[3] for the detection of bromide ion in water was established as a test for free bromine. Calibration curves have been prepared at 2°, 10°, 20°, 30°, and 40°C (figure 4). The reaction is not temperature dependent in the range 2°-30°C, but at 40°C the results obtained were approximately 5% low. In the range 2°-40°C, nitrite manganic manganese, chloramine, and free chlorine do not interfere.

3. "Standard Methods for the Examination of Water and Wastewater", APHA, 12th Edition, pp.66-7 (1965).

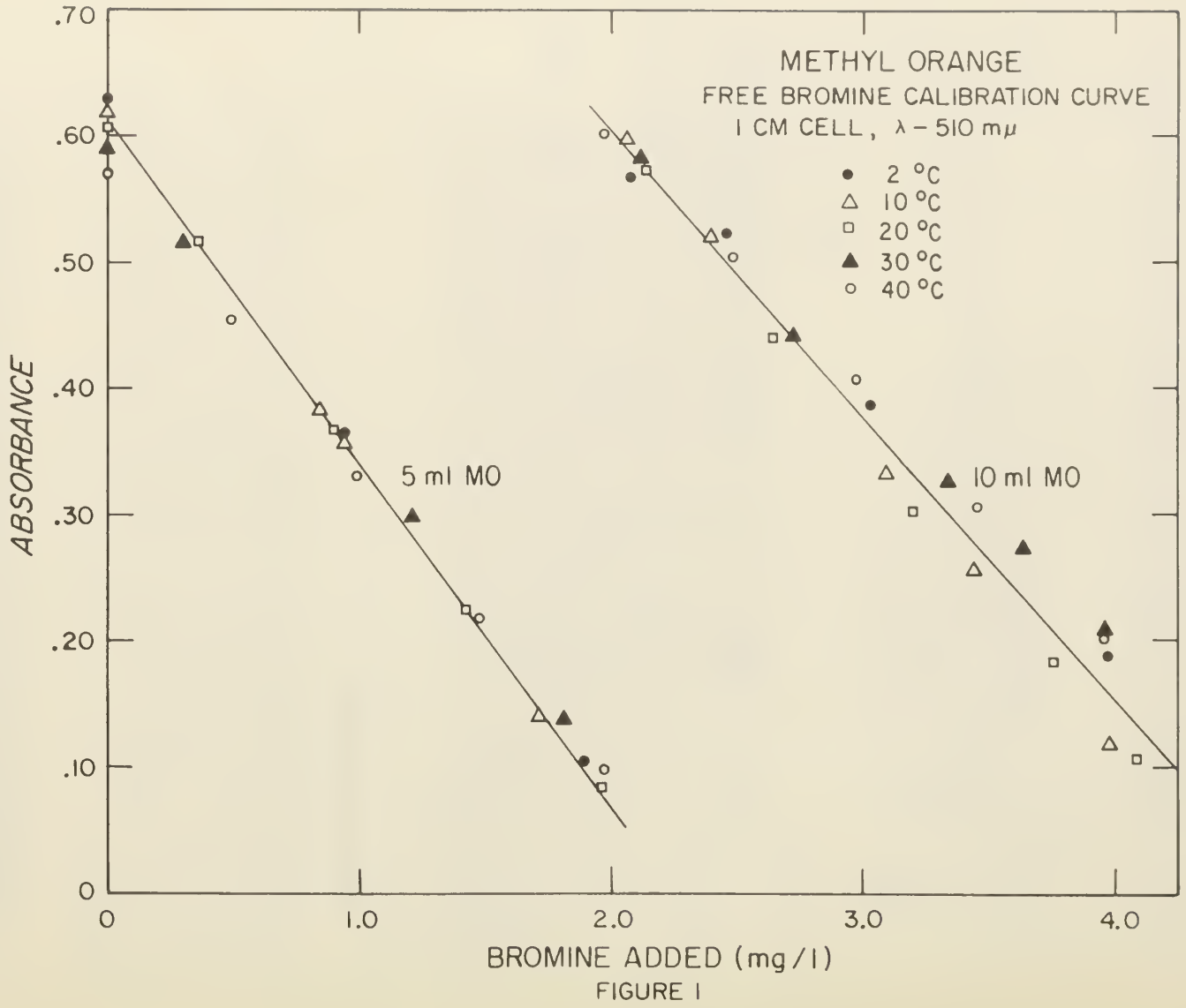
METHYL ORANGE
FREE BROMINE CALIBRATION CURVE
1 CM CELL, λ – 510 mμ
2 °C
10 °C
20 °C
30 °C
40 °C
5 ml MO
10 ml MO
ABSORBANCE
.70
.60
.50
.40
.30
.20
.10
0
0
1.0
2.0
3.0
4.0
BROMINE ADDED (mg/l)

FIGURE 1

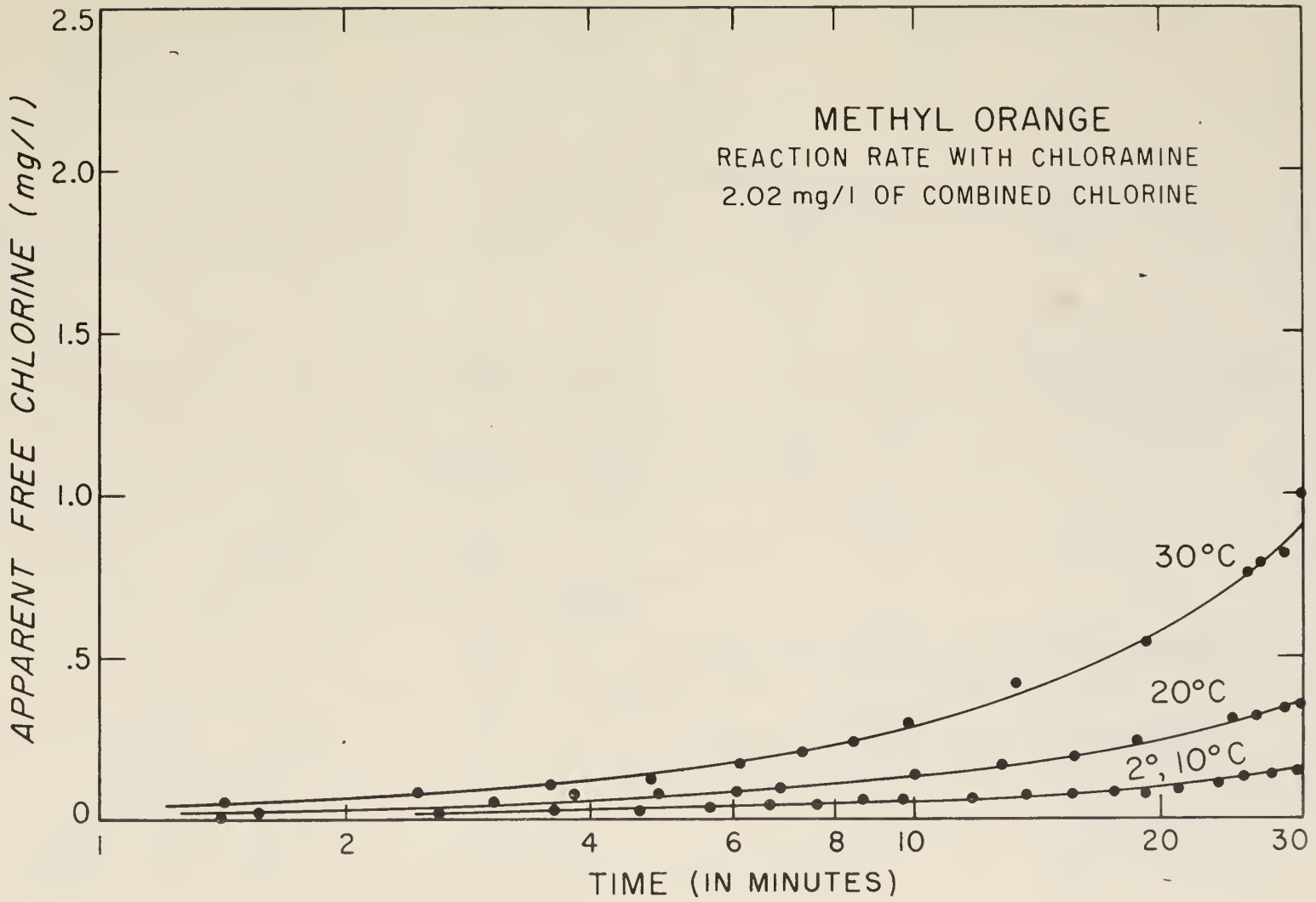
METHYL ORANGE
REACTION RATE WITH CHLORAMINE
2.02 mg/l OF COMBINED CHLORINE
APPARENT FREE CHLORINE (mg/l)
2.5
2.0
1.5
1.0
.5
0
30°C
20°C
2°, 10°C
1
2
4
6
8
10
20
30
TIME (IN MINUTES)

FIGURE 2

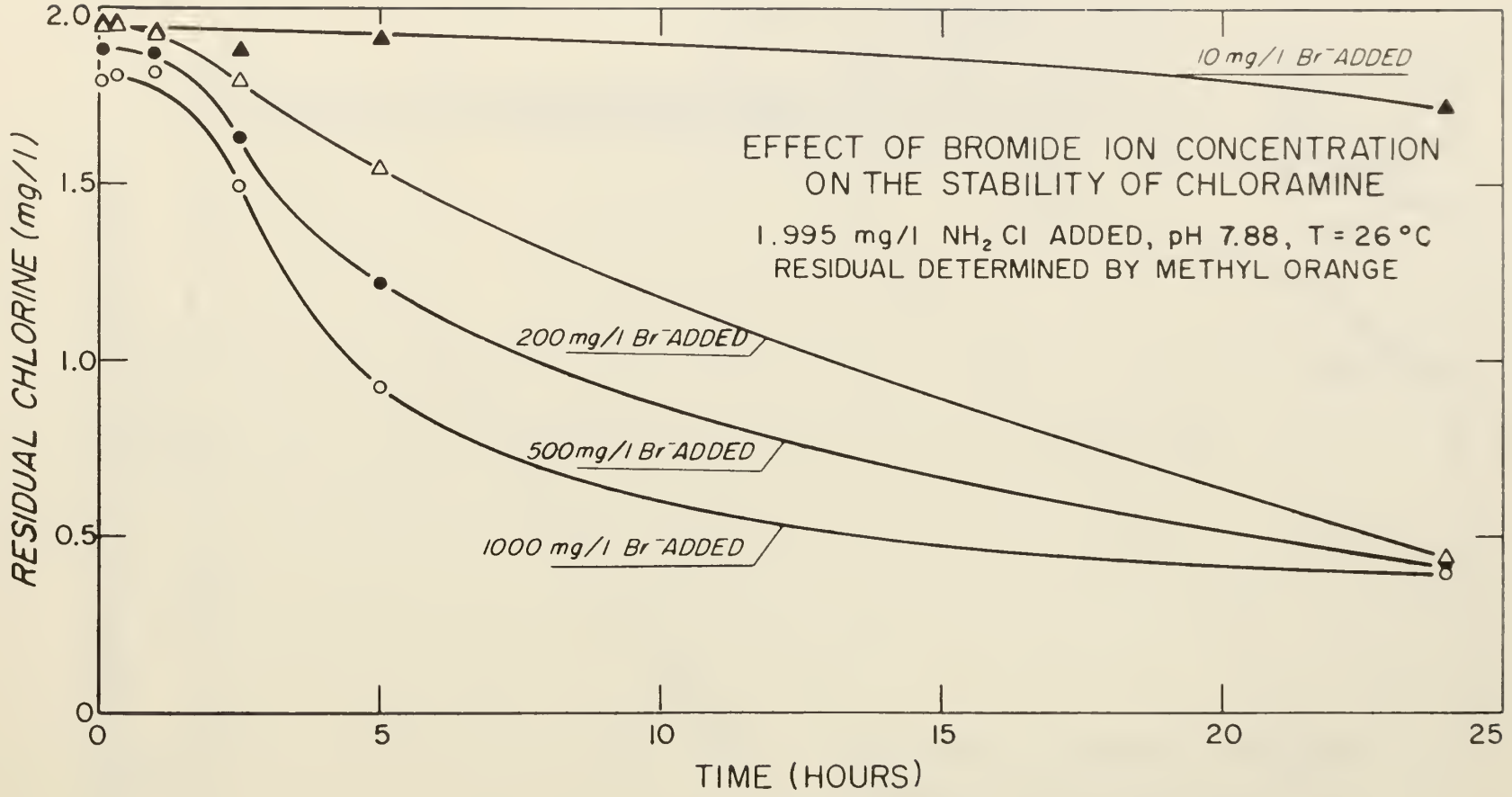
EFFECT OF BROMIDE ION CONCENTRATION
ON THE STABILITY OF CHLORAMINE
1.995 mg/l NH_2Cl ADDED, pH 7.88, T = 26 °C
RESIDUAL DETERMINED BY METHYL ORANGE
10 mg/l Br^- ADDED
200 mg/l Br^- ADDED
500 mg/l Br^- ADDED
1000 mg/l Br^- ADDED
RESIDUAL CHLORINE (mg/l)
TIME (HOURS)
2.0
1.5
1.0
0.5
0
0
5
10
15
20
25

FIGURE 3

Ferric iron interference may be considered negligible. Monobromamine reacts immediately with phenol red at 30°&40°C. At lower temperatures the interference is extreme and increases with time (figure 5).

The phenol red test was used in the preparation of the bromine-ammonia breakpoint curves shown in figures 16 to 19 of this report. The reagent performed well for the determination of total bromine, but when used as a free bromine test, considerable interference from bromamine may be observed. Bromamine interference may be reduced by the addition of 200 mg/l $NaASO_2$ within 15 seconds after the sample is added to the mixed phenol red reagent and buffer.

Reagents:

(1) 10 mg phenol red dissolved in 1 ml 0.1N NaOH and diluted to 100 ml with double distilled H_2O
(2) Buffer (pH 5.07) - 150 ml 0.5 M. $NaC_2H_3O_2$ and 100 ml 0.5 M. CH_3COOH
(3) 1.0% $NaAsO_2$

Procedure:

To determine free bromine, a 50 ml sample is added to 2 ml 0.01% phenol red and 2 ml buffer, and mixed. Within 15 seconds after mixing, 1 ml 1.0% $NaAsO_2$ is added and the absorbance determined immediately at 598 mμ, pH 5.14.

To determine total bromine, a 50 ml sample is added to 2 ml 0.01% phenol red, 2 ml buffer, and mixed. After 10 min. the absorbance is determined at 598 mμ, pH 5.14.

3. Brom Cresol Purple (BCP)

Brom cresol purple calibration curves have been prepared at the following temperatures: 2°, 10°, 20°, 30°, and 40°C. The curves are non-linear, particularly at concentrations below 1 mg/l, and show some temperature dependence in the range of 2-5 ppm Br_2 (figure 6). Manganic manganese, ferric iron, and nitrite interferences were checked at these temperatures as well as monobromamine, monochloramine, and free chlorine. Interference from manganic manganese, nitrite, monobromamine, and monochloramine may be considered negligible. Ferric iron produces a slight interference (figure 7). Free chlorine produces an appreciable interference (figure 8).

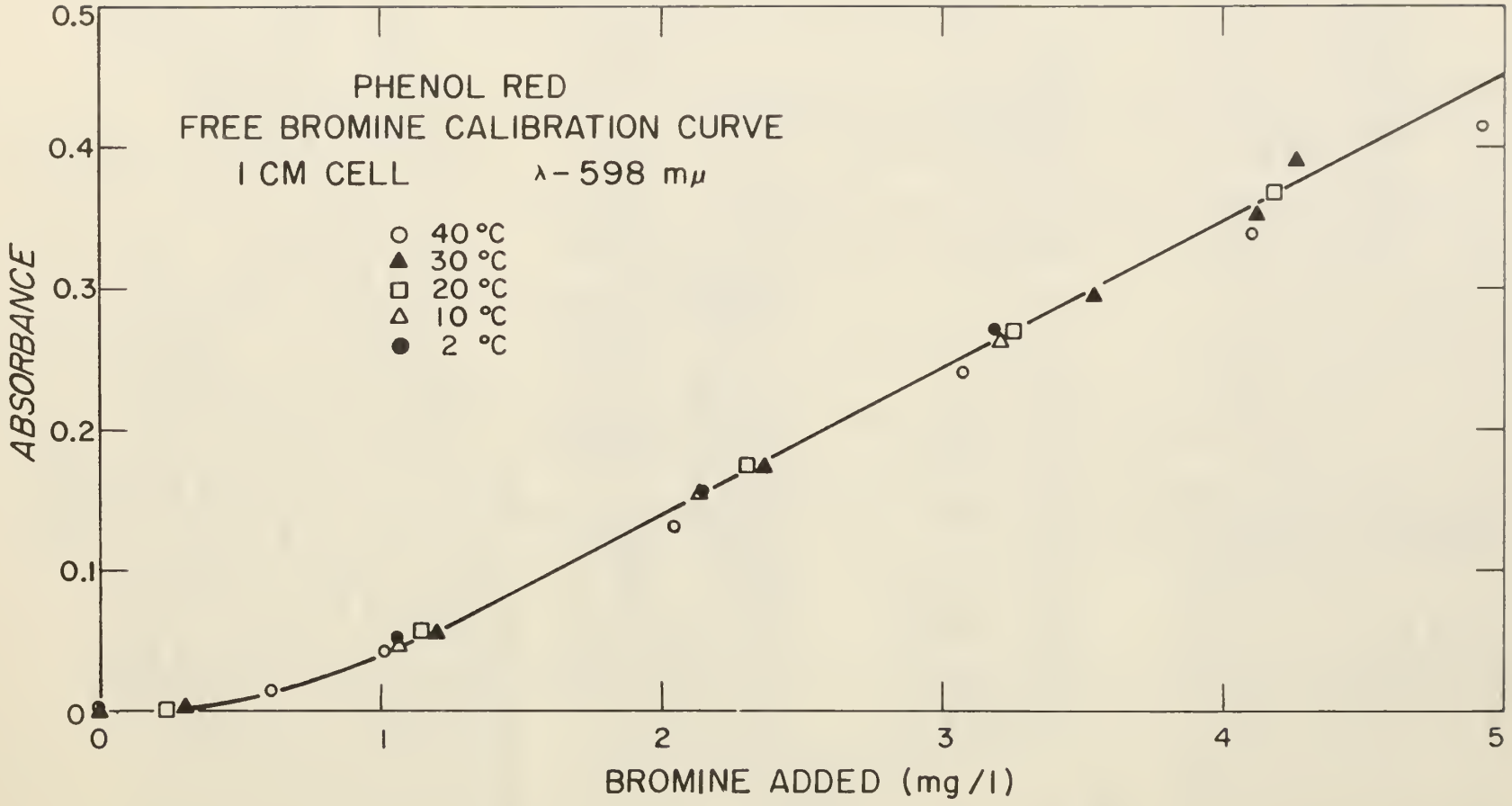
PHENOL RED
FREE BROMINE CALIBRATION CURVE
1 CM CELL λ - 598 mμ
40 °C
30 °C
20 °C
10 °C
2 °C
ABSORBANCE
0.5
0.4
0.3
0.2
0.1
0
0
1
2
3
4
5
BROMINE ADDED (mg/l)

FIGURE 4

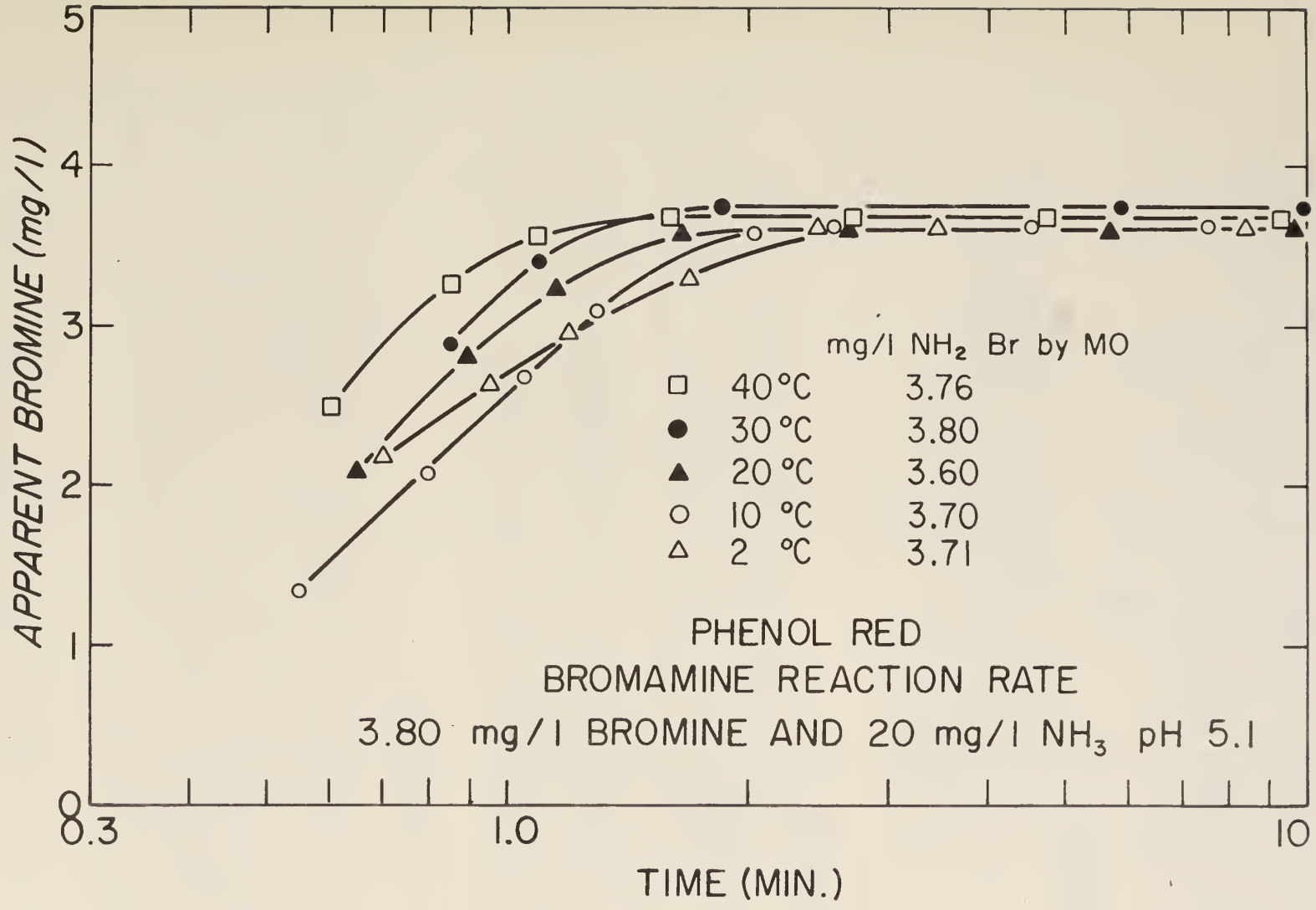
APPARENT BROMINE (mg/l)
5
4
3
2
1
0
0.3
1.0
10
TIME (MIN.)
mg/l NH2 Br by MO
40°C 3.76
30°C 3.80
20°C 3.60
10°C 3.70
2°C 3.71
PHENOL RED
BROMAMINE REACTION RATE
3.80 mg/l BROMINE AND 20 mg/l NH3 pH 5.1

FIGURE 5

Free chlorine interference may be reduced by the addition of 200 mg/l $NaAsO_2$ at 1 minute contact time. Earlier addition of $NaAsO_2$ may prevent complete reaction of the free available bromine. Free Br_2 + free Cl_2 may be determined by the addition of 200 mg/l bromide ion to the sample before testing.

The BCP reagent is known to be stable for at least one month.

Reagents:

(1) 0.0125% BCP, sodium salt. (Reagent was dried at 103°C for 1 hr. before preparation)
(2) Buffer solution (pH 9.0) - 250 ml 0.50 M $NaHCO_3$+20 ml 1.0 M NaOH
(3) 20,000 mg/l Br- (from NaBr)
(4) 1.0% $NaAsO_2$

Procedure:

(1) To determine free bromine concentration, a 50 ml sample is added with mixing, to 3 ml 0.0125% BCP and 5 ml buffer solution. After 1 minute, 1 ml $NaAsO_2$ solution is added, and the solution is mixed well. The absorbance of the resulting solution is determined immediately at 595 mμ, pH 9.35.

(2) To determine the combined free bromine and free chlorine concentration (as free bromine), 0.5 ml Br- solution is added to a 50 ml sample and thoroughly mixed. The sample is then added, with mixing, to 3 ml 0.0125% BCP and 5 ml buffer, and after 1 minute the absorbance is determined at 595 mμ, as before.

4. Phenosafranin

The reaction between free bromine and phenosafranin does not appear to be temperature dependent in the range 2°-40°C. Calibration curves have been prepared at 2°, 10°, 20°, 30°, and 40°C, as shown in figure 9. Interferences have also been checked at these temperatures. Manganic manganese, ferric iron, nitrite, and chloramine interferences are negligible. Monobromamine produces a slight interference after 2 minutes and therefore may be eliminated by determining absorbance immediately (figure 10). Free chlorine produces a serious interference, as is shown in figure 11.

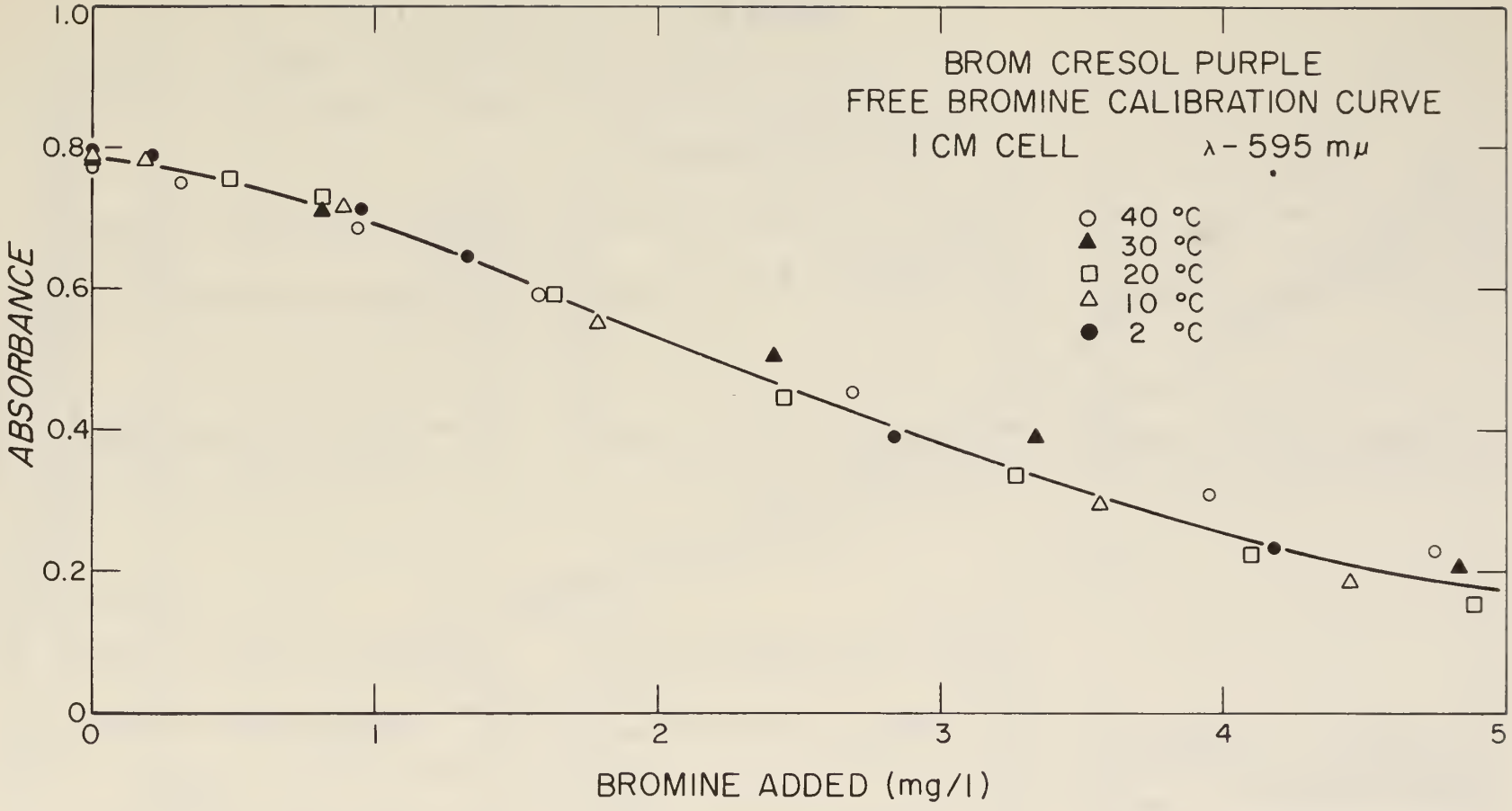
BROM CRESOL PURPLE
FREE BROMINE CALIBRATION CURVE
1 CM CELL
λ - 595 mμ
40 °C
30 °C
20 °C
10 °C
2 °C
ABSORBANCE
1.0
0.8
0.6
0.4
0.2
0
0
1
2
3
4
5
BROMINE ADDED (mg/l)

FIGURE 6

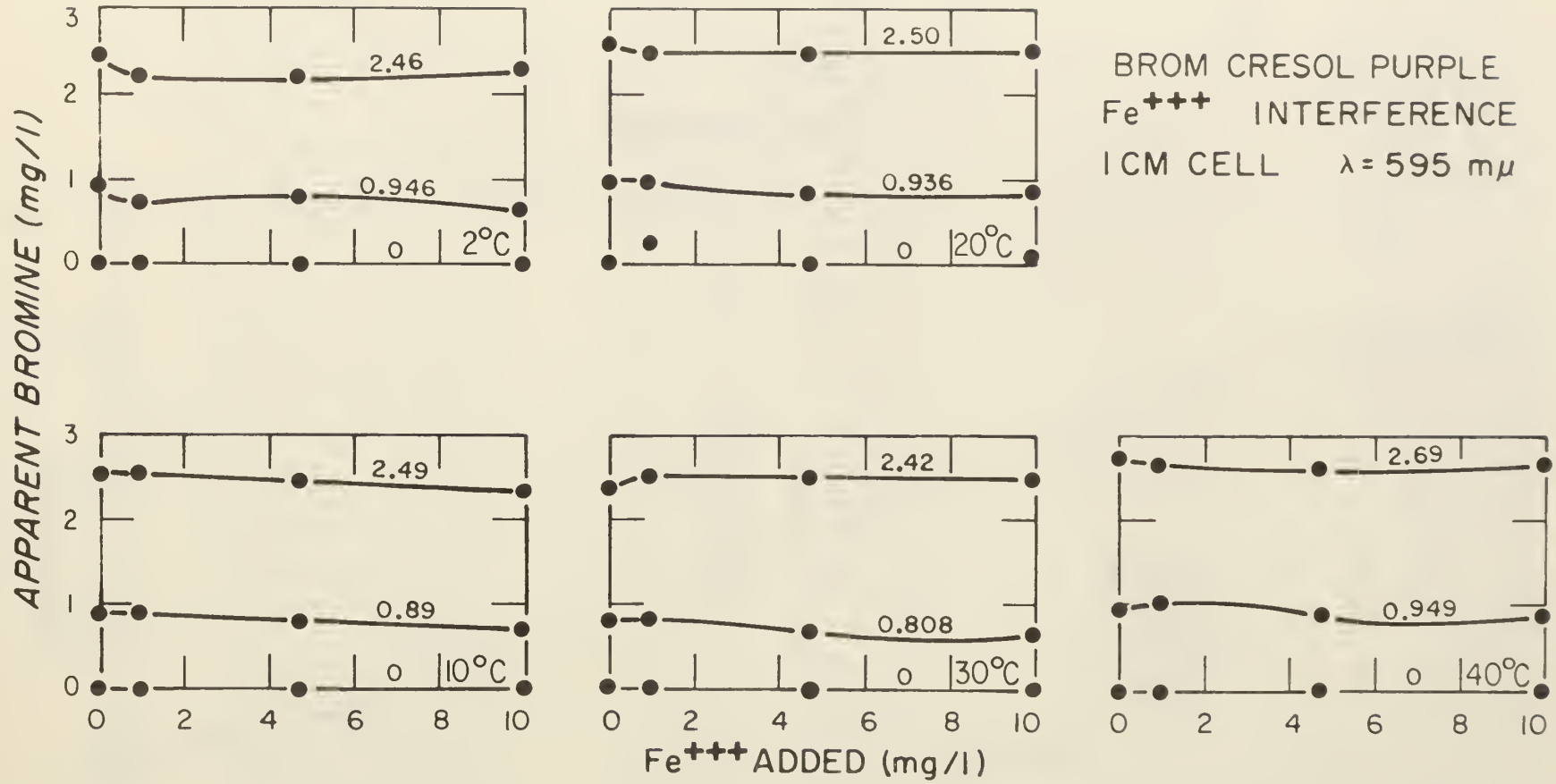
APPARENT BROMINE (mg/l)
3
2
1
0
2.46
0.946
2°C
2.50
0.936
20°C
2.49
0.89
10°C
2.42
0.808
30°C
2.69
0.949
40°C
0 2 4 6 8 10
Fe+++ ADDED (mg/l)
BROM CRESOL PURPLE
Fe+++ INTERFERENCE
ICM CELL λ = 595 mμ

FIGURE 7

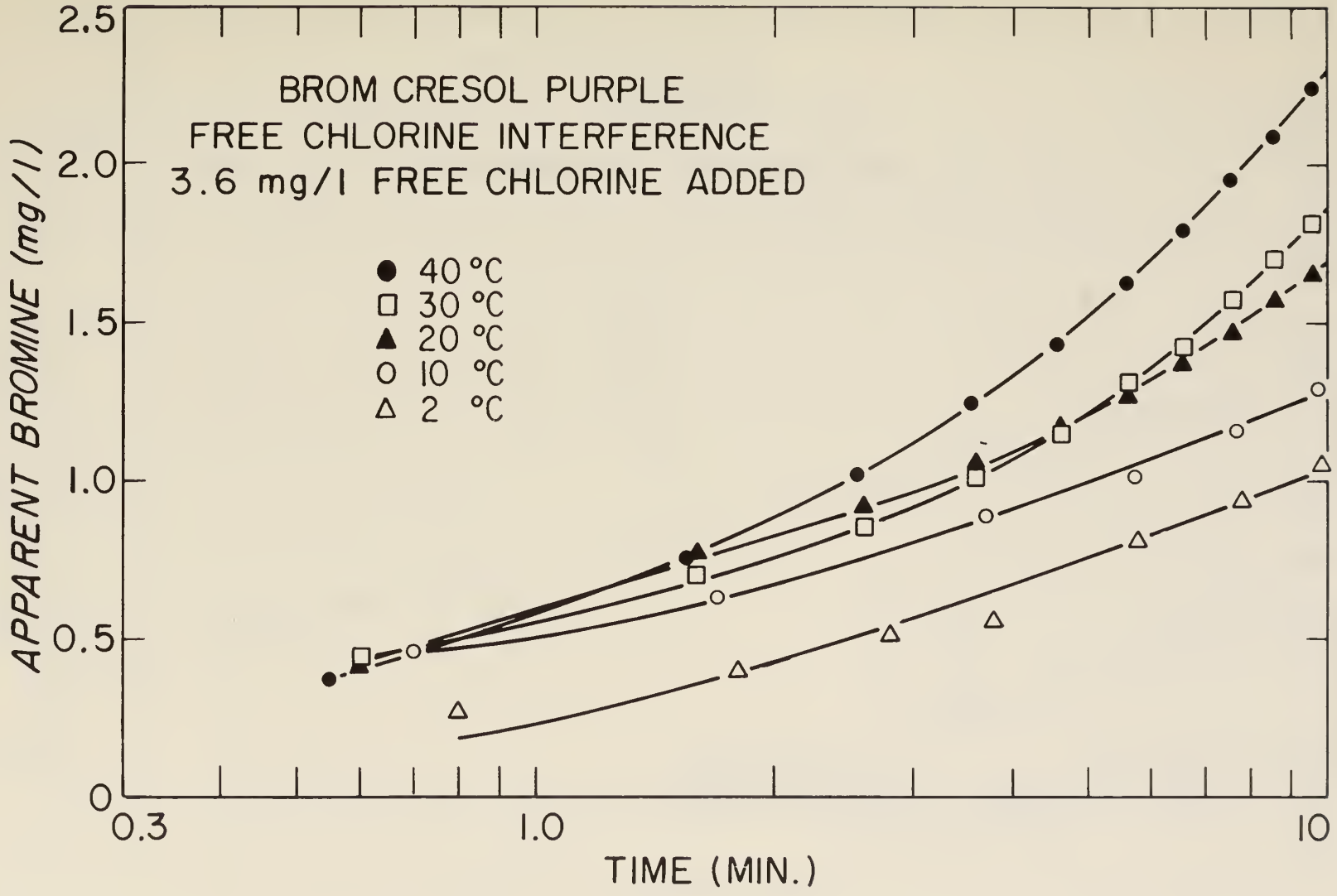
BROM CRESOL PURPLE
FREE CHLORINE INTERFERENCE
3.6 mg/l FREE CHLORINE ADDED
40 °C
30 °C
20 °C
10 °C
2 °C
APPARENT BROMINE (mg/l)
TIME (MIN.)
2.5
2.0
1.5
1.0
0.5
0
0.3
1.0
10

FIGURE 8

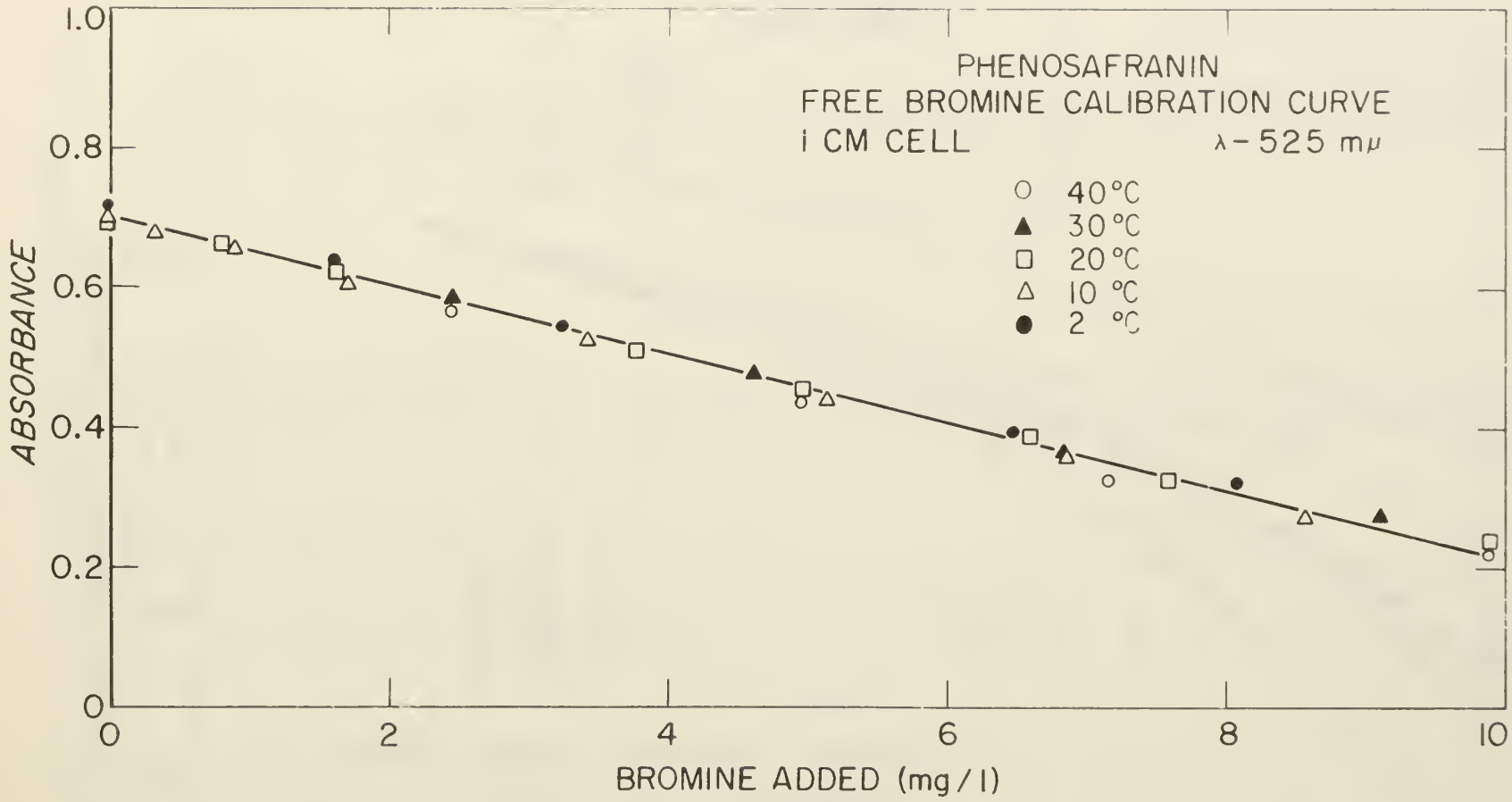
PHENOSAFRANIN
FREE BROMINE CALIBRATION CURVE
1 CM CELL
λ - 525 mμ
40 °C
30 °C
20 °C
10 °C
2 °C
ABSORBANCE
1.0
0.8
0.6
0.4
0.2
0
0
2
4
6
8
10
BROMINE ADDED (mg/l)

FIGURE 9

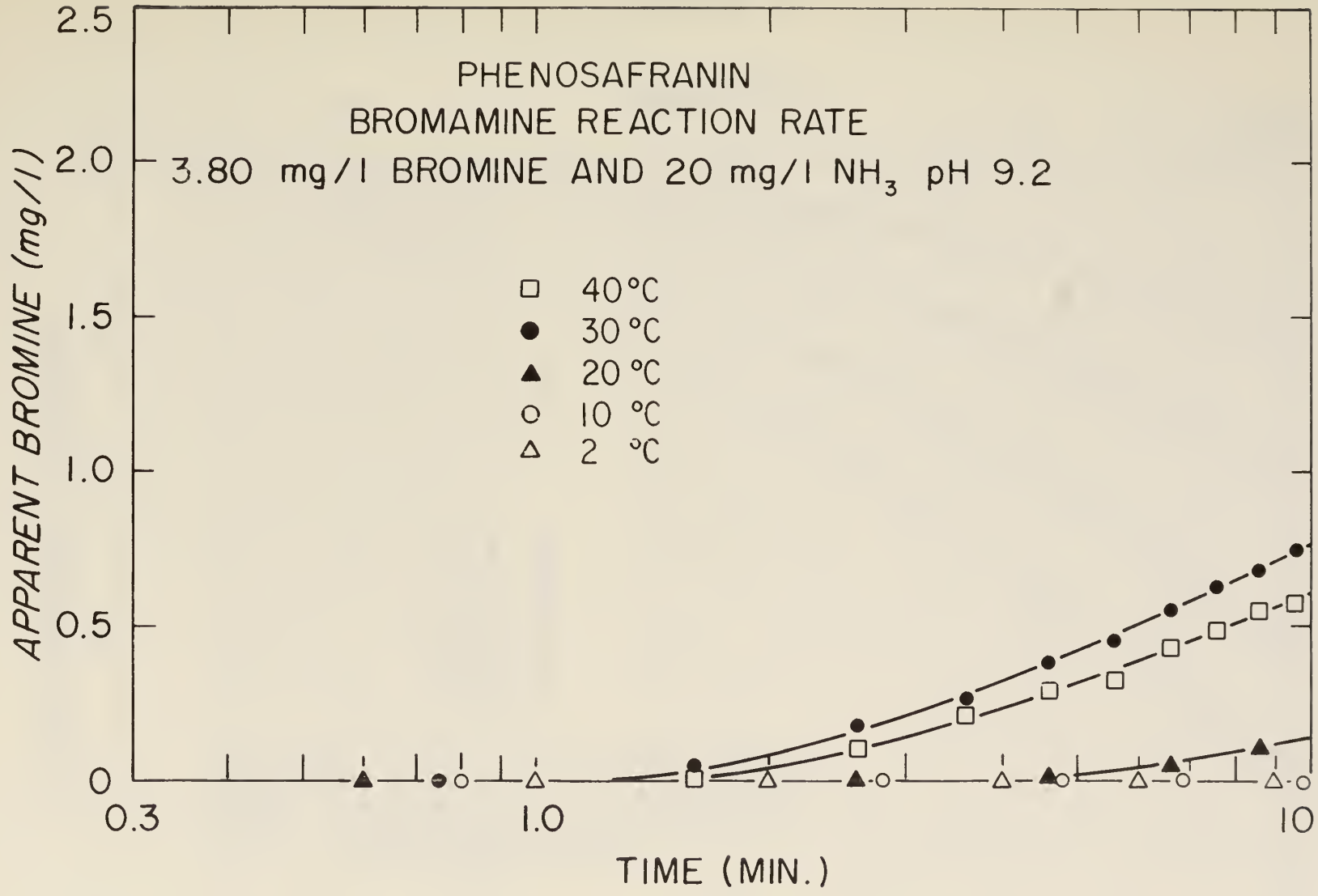
PHENOSAFRANIN
BROMAMINE REACTION RATE
3.80 mg/l BROMINE AND 20 mg/l NH_3 pH 9.2
40°C
30°C
20°C
10°C
2°C
APPARENT BROMINE (mg/l)
2.5
2.0
1.5
1.0
0.5
0
0.3
1.0
10
TIME (MIN.)

FIGURE 10

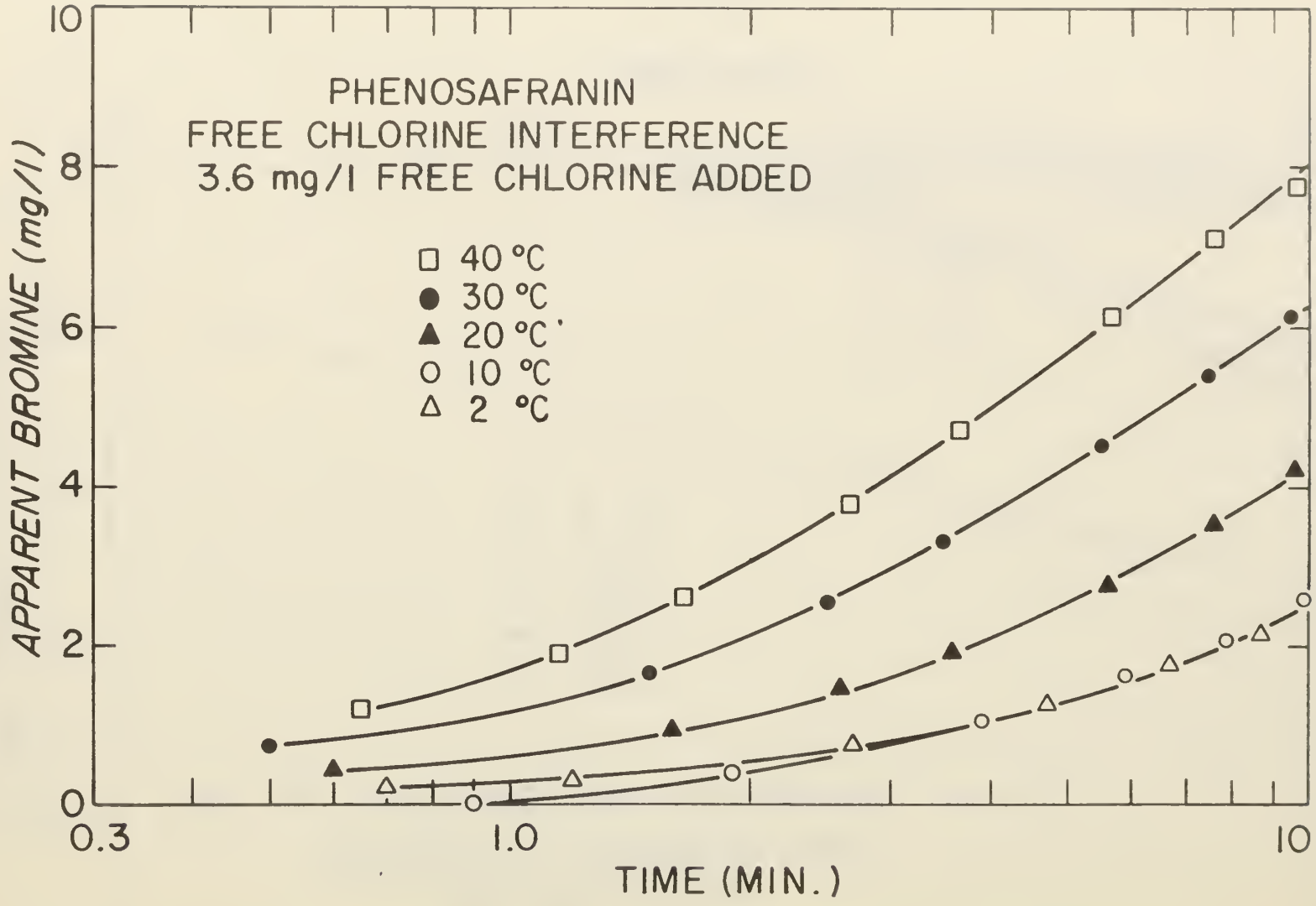
PHENOSAFRANIN
FREE CHLORINE INTERFERENCE
3.6 mg/l FREE CHLORINE ADDED
40 °C
30 °C
20 °C
10 °C
2 °C
APPARENT BROMINE (mg/l)
TIME (MIN.)
0
2
4
6
8
10
0.3
1.0
10

FIGURE 11

to 19). The ammonia-bromine reaction appears to be similar to the ammonia-chlorine reaction. The bromamine breakpoint requires 14 mg/l free bromine, while the chloramine breakpoint requires 6 mg/l free Cl_2 for oxidation of 1 mg/l of NH_3. These are equivalent on a molar basis. The bromine-ammonia reaction is generally faster than the chlorine-ammonia reaction, especially at pH 9.2; the reaction of either halogen with ammonia is slow at pH 4.9. It may be observed that amine stability is better for chlorine than for bromine.

Methyl orange and neutral orthotolidine were the reagents used in preparing the chlorine breakpoint curves. Both reagents may be used for the measurement of free and of total residual chlorine. Methyl orange, phenol red, and brom cresol purple were the tests used in preparing the bromine curves. Phenol red and brom cresol purple were used for free bromine determinations, and phenol red and methyl orange for the determination of total bromine.

Samples were prepared by the addition of the desired concentration of free bromine or chlorine to a buffered solution containing NH_3 while mixing on a magnetic stirrer. The samples were stored in glass stoppered bottles and samples extracted periodically for testing. Tests run at a given contact time were performed as nearly simultaneously as possible, but there was a time lapse of from 3 to 5 minutes from the addition of the sample for the first test to the addition of the sample for the fourth test. This may account for some variation in results with different tests, especially at short contact times.

E. STUDIES OF BROMAMINE STABILITY

A major source of difficulty in working with bromamine solutions stems from their extreme instability. A series of stability tests were carried out at room temperature with varying ammonia-to-bromine ratios and varying pH.

The test procedure was as follows: Free bromine (as NaOBr) was added to a buffered solution containing the desired concentration of ammonia. During bromine addition, samples were mixed by means of a magnetic stirrer to insure complete mixing and to eliminate the possibility of error due to local excesses of bromine or ammonia. At specified time intervals, samples were withdrawn and analyzed for total bromine using the Methyl Orange procedure. The results of a selection of the tests may be found in figures 20 to 26.

The reagent is somewhat less sensitive than the other reagents being considered, but might be of value in instances when high bromine concentrations are to be determined.

Reagents:

(1) 0.01% phenosafranin
(2) Buffer (pH 9.18) - 0.042 M borax
(3) 1.0% $NaAsO_2$

Procedure:

A 50 ml sample is added to 3 ml 0.01% phenosafranin and 5 ml buffer and mixed well. After 15 seconds 1 ml 1.0% $NaAsO_2$ is added. Absorbance is determined immediately at 525 mμ, pH 9.2.

C. NOTES ON MANGANESE INTERFERENCE

In checking the interference due to the manganic ion in the brom cresol purple and phenol red tests, no manganese interference was observed when Br_2 was not present in the sample. However, in samples containing both bromine and manganese, there appeared to be negative interference due to manganese. The same effect was observed when free bromine was determined by means of the arsenite modification of the DPD test on a sample containing both bromine and manganese.

It may be shown that free bromine oxidizes Mn^{+2}. This was checked using the phenol red test. A sample of Mn^{+2} and Br_2 of known concentrations in buffered solution was prepared and the sample tested periodically for loss of Br_2. At pH 5.15 and pH 6.17, free bromine did not oxidize Mn^{+2}. However, at pH 8.4 and above free bromine in moderate excess slowly oxidized the manganese ion. The product of this oxidation is not entirely Mn^{+4}.

Since the manganic ion was prepared for use in these tests by air oxidation at pH 10, it appears probable that the negative interference found in the phenol red and brom cresol purple methods was not a true interference but a consumption of bromine in further oxidation of the manganese ion at the high pH used in the test.

D. THE BREAKPOINT REACTION FOR FREE BROMINE

Curves showing bromine and chlorine breakpoint phenomena for water with an ammonia concentration of 1 mg/l have been prepared at pH 9.2, 8.4, 7.2, and 4.9 (figures 12

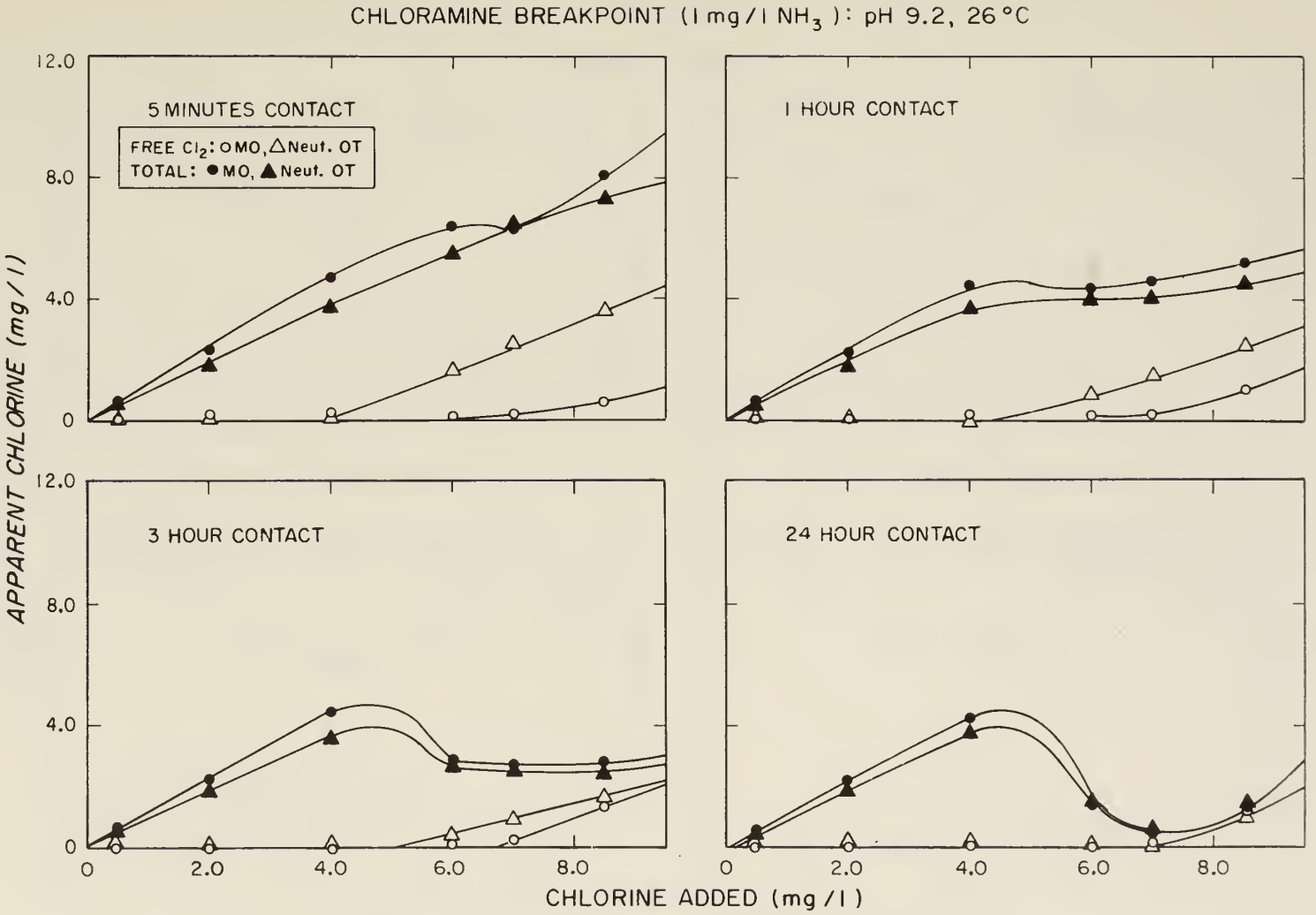
CHLORAMINE BREAKPOINT (1 mg/l NH_3): pH 9.2, 26 °C
5 MINUTES CONTACT
FREE Cl_2: ○ MO, △ Neut. OT
TOTAL: ● MO, ▲ Neut. OT
1 HOUR CONTACT
3 HOUR CONTACT
24 HOUR CONTACT
APPARENT CHLORINE (mg/l)
CHLORINE ADDED (mg/l)
0
2.0
4.0
6.0
8.0
12.0

FIGURE 12

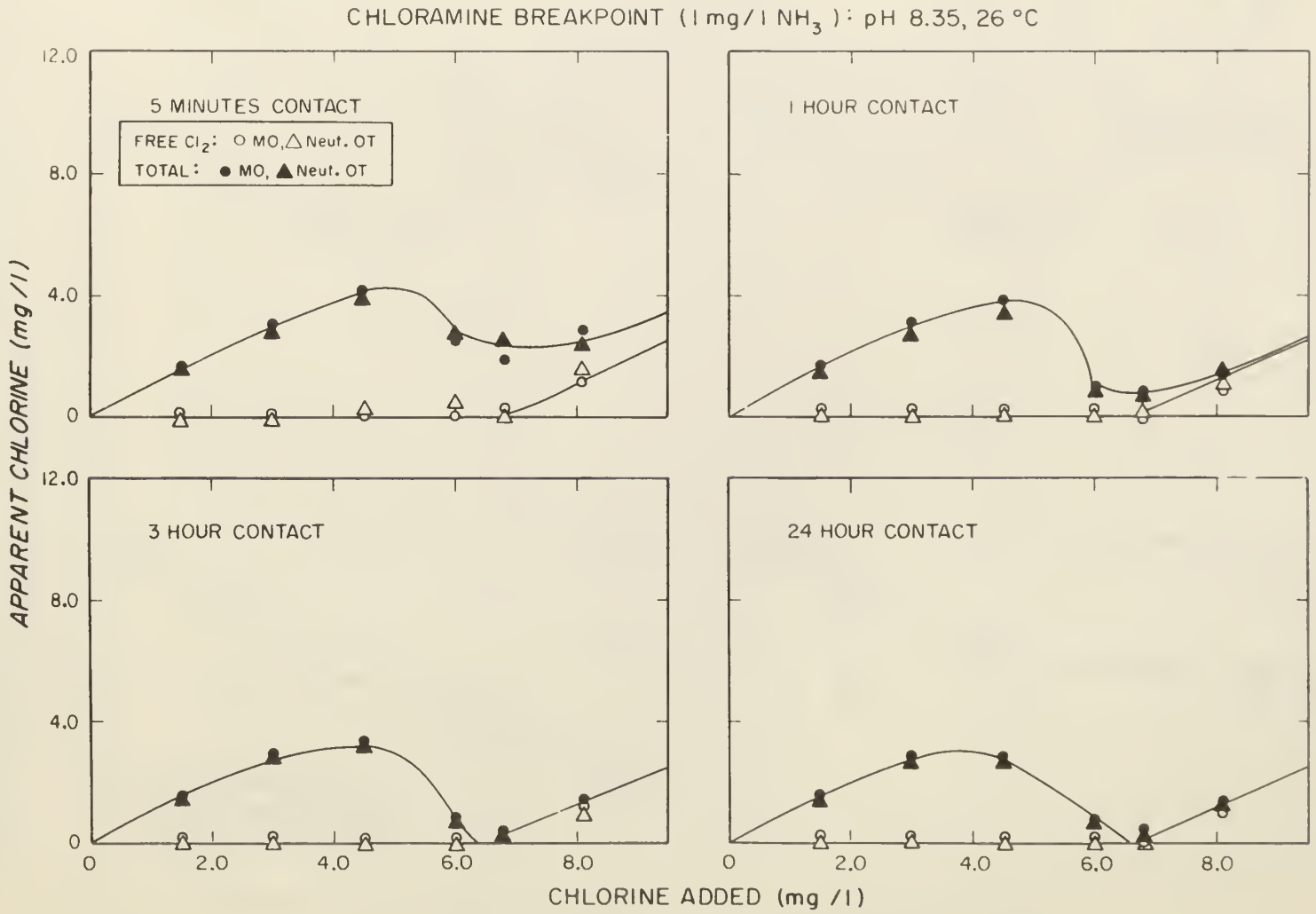
CHLORAMINE BREAKPOINT (1 mg/l NH_3): pH 8.35, 26 °C
5 MINUTES CONTACT
FREE Cl_2: ○ MO, △ Neut. OT
TOTAL: ● MO, ▲ Neut. OT
1 HOUR CONTACT
3 HOUR CONTACT
24 HOUR CONTACT
APPARENT CHLORINE (mg/l)
CHLORINE ADDED (mg/l)
0
2.0
4.0
6.0
8.0
12.0

FIGURE 13

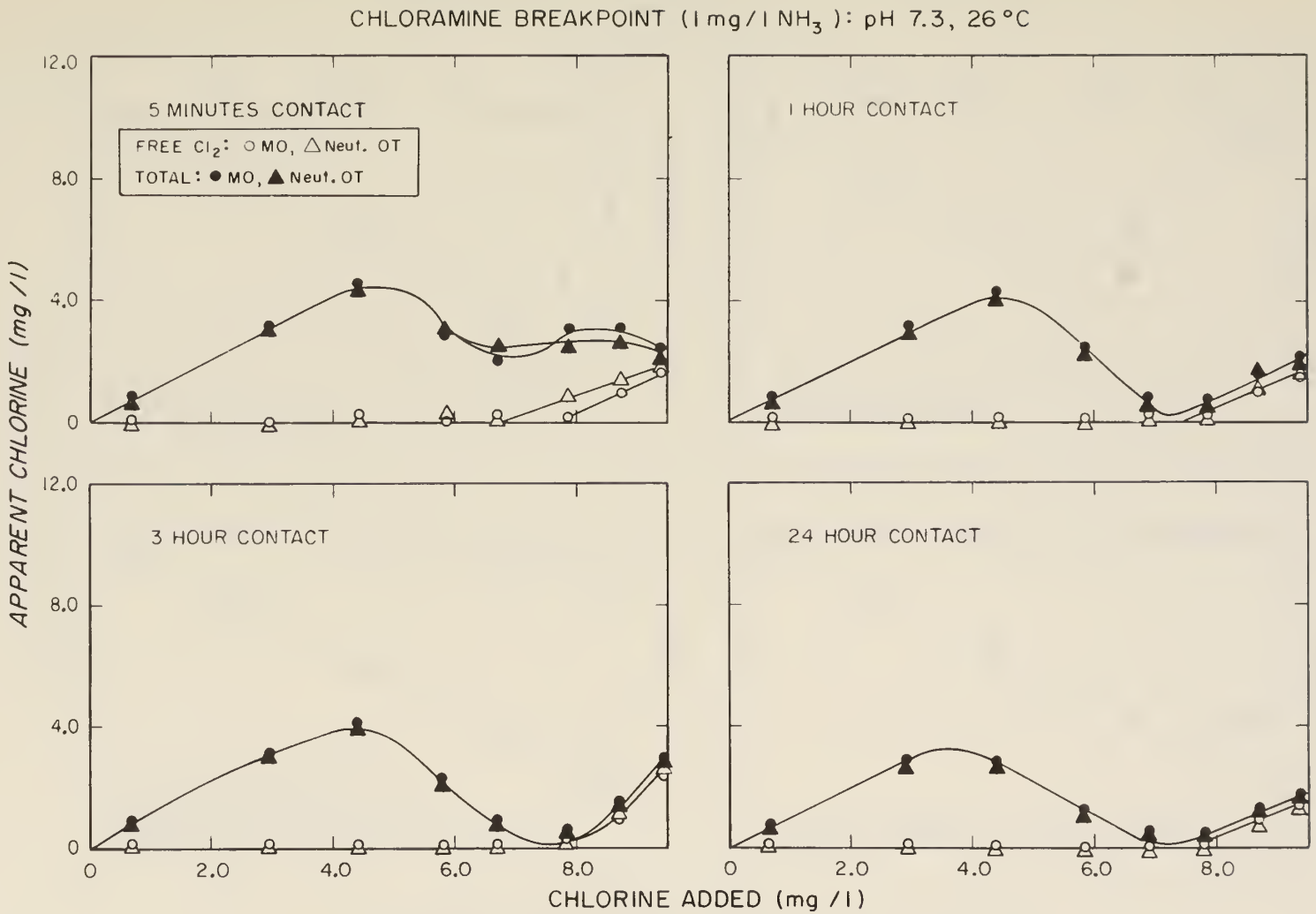
CHLORAMINE BREAKPOINT (1 mg/l NH_3): pH 7.3, 26 °C
5 MINUTES CONTACT
FREE Cl_2: ○ MO, △ Neut. OT
TOTAL: ● MO, ▲ Neut. OT
1 HOUR CONTACT
3 HOUR CONTACT
24 HOUR CONTACT
APPARENT CHLORINE (mg/l)
CHLORINE ADDED (mg/l)
0
2.0
4.0
6.0
8.0
12.0

FIGURE 14

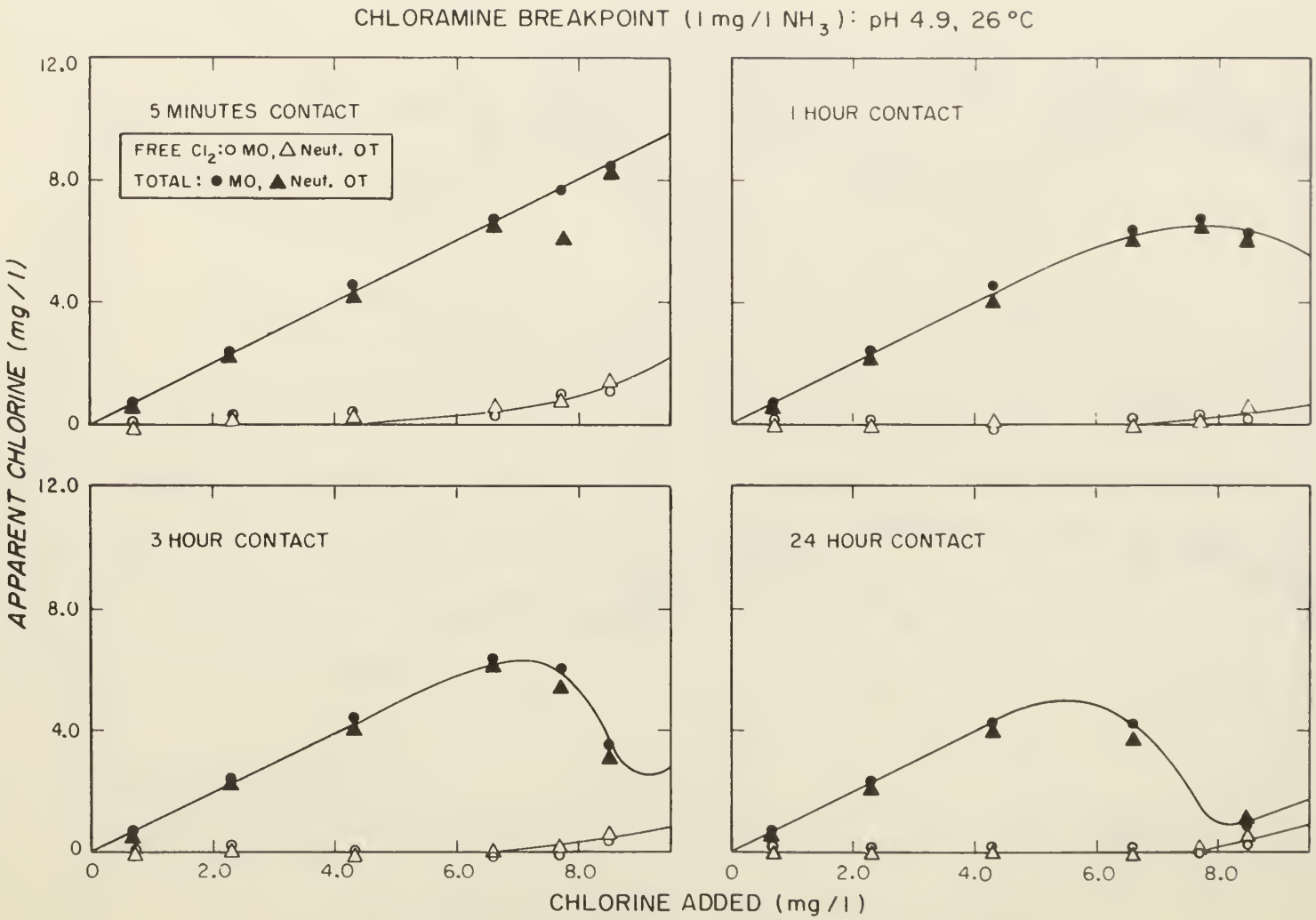
CHLORAMINE BREAKPOINT (1 mg/l NH_3): pH 4.9, 26 °C
5 MINUTES CONTACT
FREE Cl_2: ○ MO, △ Neut. OT
TOTAL: ● MO, ▲ Neut. OT
1 HOUR CONTACT
3 HOUR CONTACT
24 HOUR CONTACT
APPARENT CHLORINE (mg/l)
CHLORINE ADDED (mg/l)
0
2.0
4.0
6.0
8.0
12.0

FIGURE 15

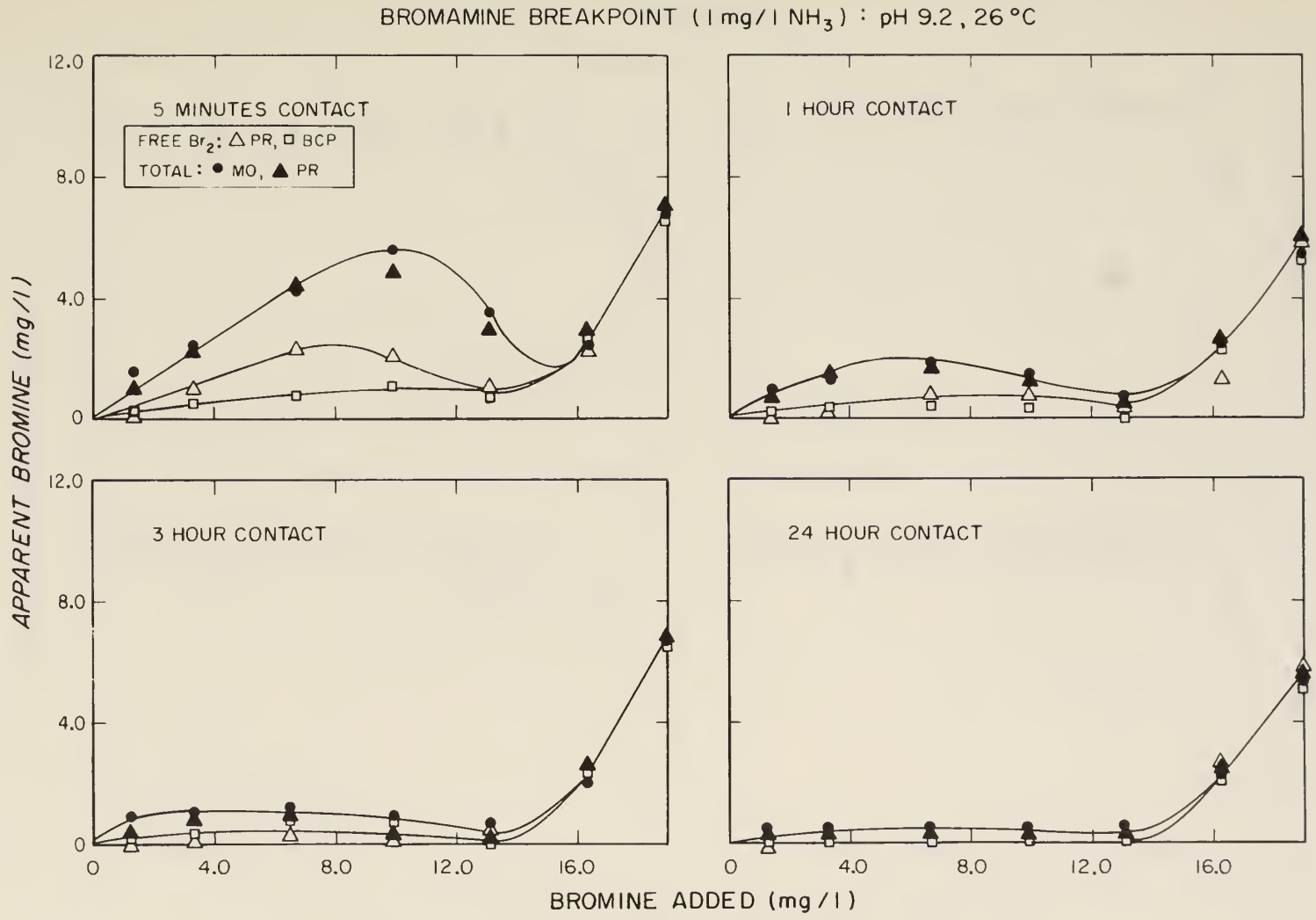
BROMAMINE BREAKPOINT (1 mg/l NH_3) : pH 9.2, 26 °C
5 MINUTES CONTACT
FREE Br_2: △ PR, □ BCP
TOTAL: ● MO, ▲ PR
1 HOUR CONTACT
3 HOUR CONTACT
24 HOUR CONTACT
APPARENT BROMINE (mg/l)
BROMINE ADDED (mg/l)
0
4.0
8.0
12.0
16.0

FIGURE 16

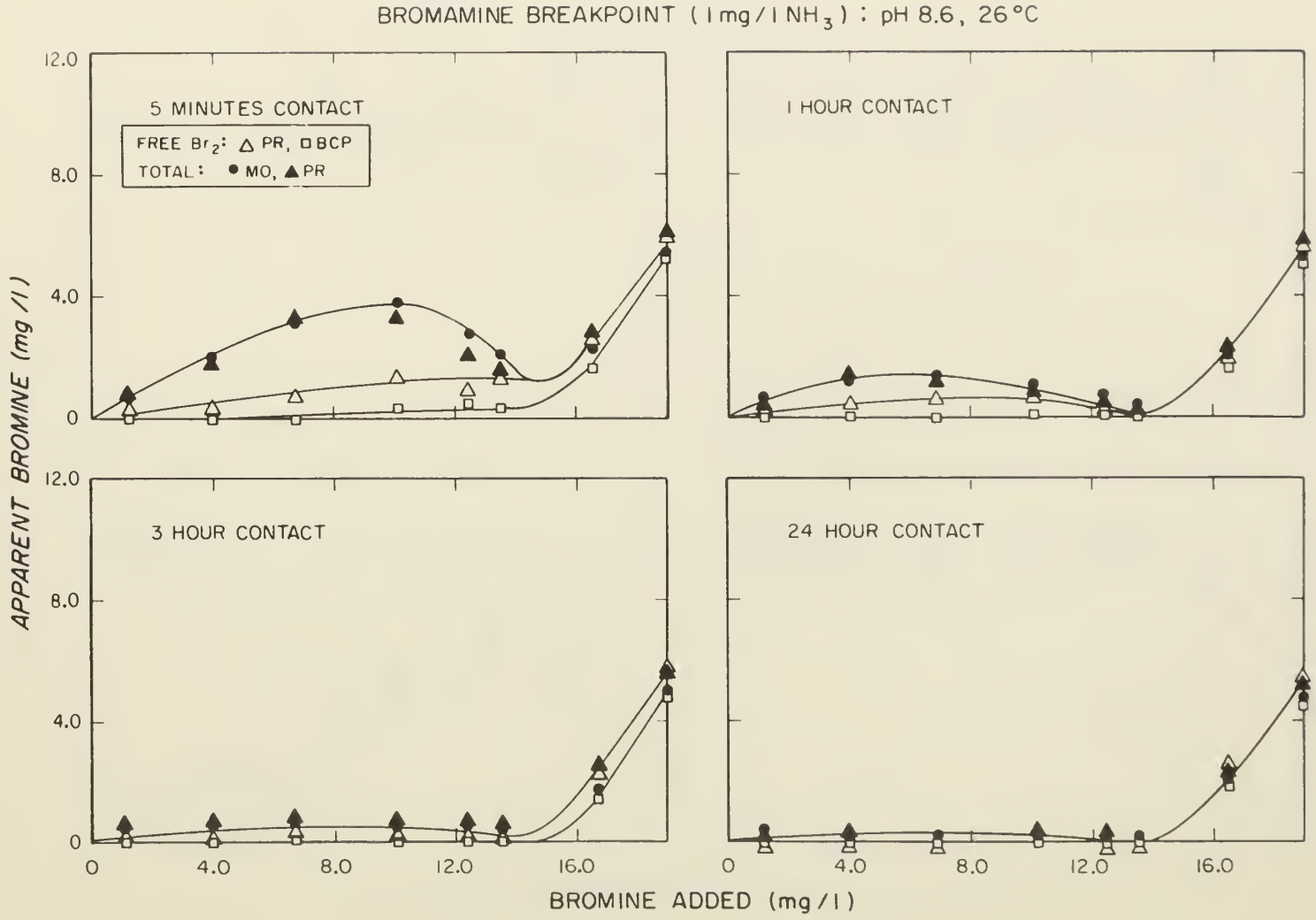
BROMAMINE BREAKPOINT (1 mg/l NH_3) : pH 8.6, 26 °C
5 MINUTES CONTACT
FREE Br_2: △ PR, □ BCP
TOTAL: ● MO, ▲ PR
1 HOUR CONTACT
3 HOUR CONTACT
24 HOUR CONTACT
APPARENT BROMINE (mg/l)
BROMINE ADDED (mg/l)
0
4.0
8.0
12.0
16.0

FIGURE 17

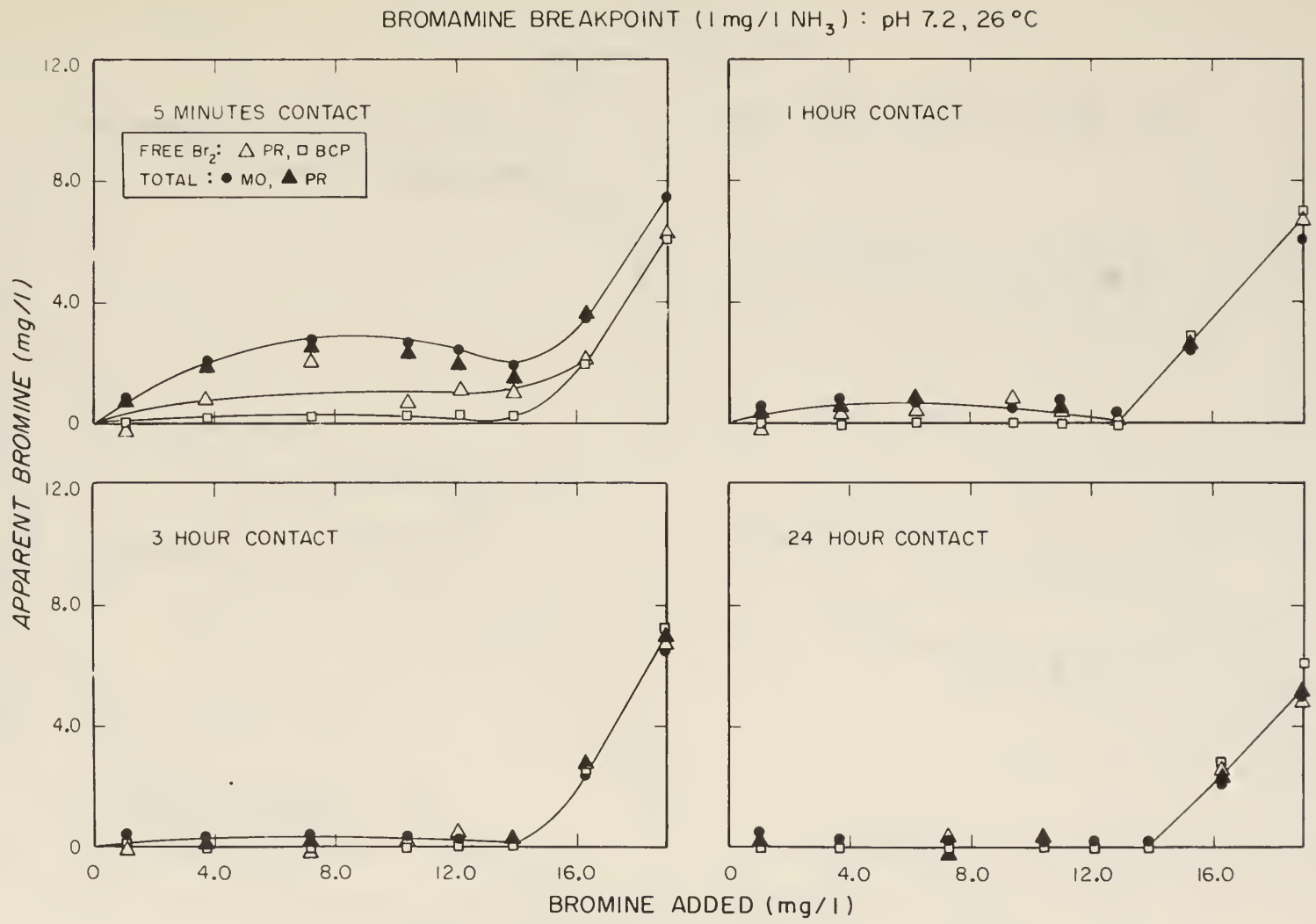
BROMAMINE BREAKPOINT (1 mg/l NH_3) : pH 7.2, 26 °C
5 MINUTES CONTACT
FREE Br_2: △ PR, □ BCP
TOTAL : ● MO, ▲ PR
1 HOUR CONTACT
3 HOUR CONTACT
24 HOUR CONTACT
APPARENT BROMINE (mg/l)
BROMINE ADDED (mg/l)
0
4.0
8.0
12.0
16.0

FIGURE 18

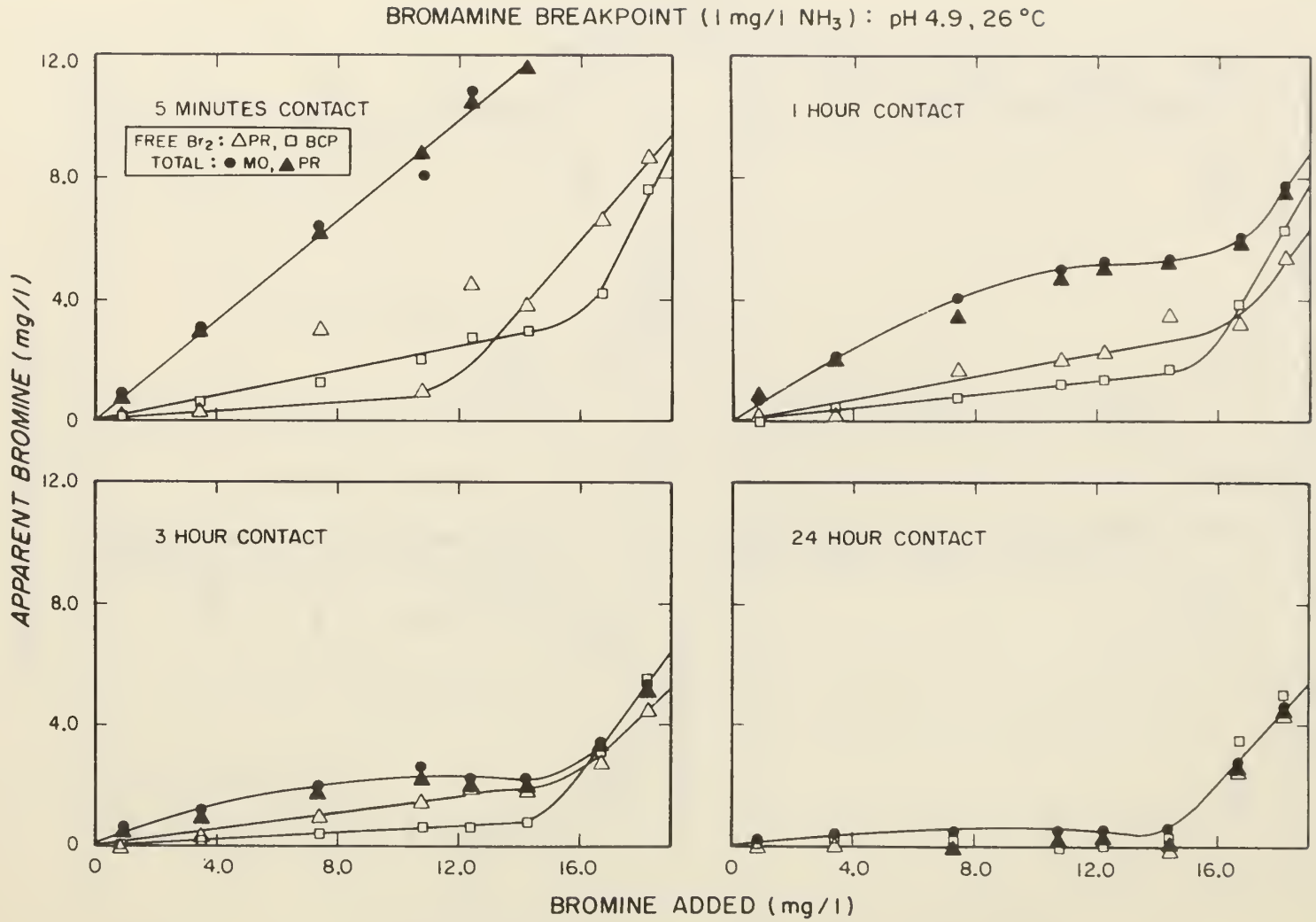
BROMAMINE BREAKPOINT (1 mg/l NH_3) : pH 4.9, 26 °C
5 MINUTES CONTACT
FREE Br_2 : △PR, □ BCP
TOTAL : ● MO, ▲ PR
1 HOUR CONTACT
3 HOUR CONTACT
24 HOUR CONTACT
APPARENT BROMINE (mg/l)
BROMINE ADDED (mg/l)
0
4.0
8.0
12.0
16.0

FIGURE 19

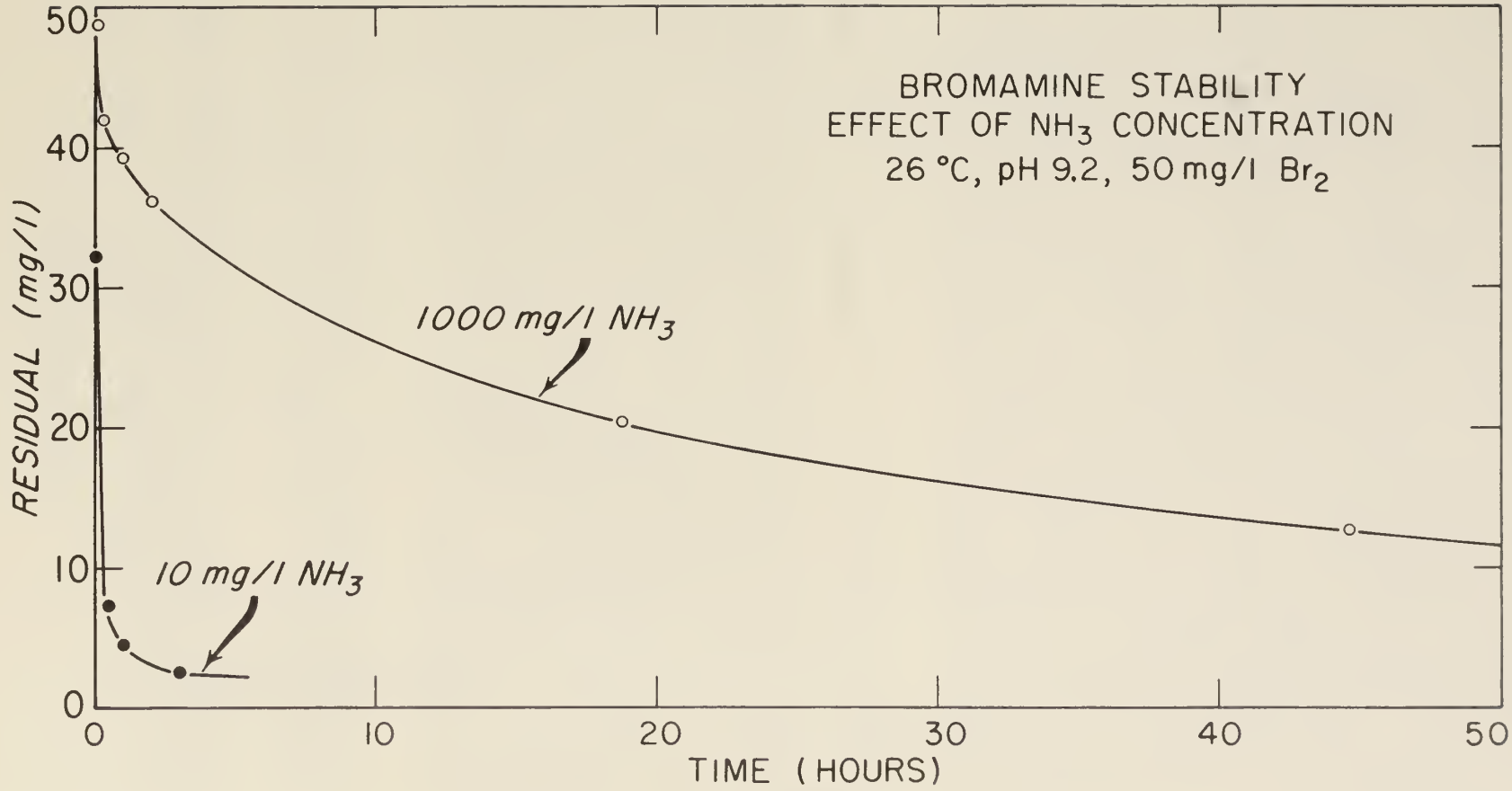
BROMAMINE STABILITY
EFFECT OF NH_3 CONCENTRATION
26 °C, pH 9.2, 50 mg/l Br_2
1000 mg/l NH_3
10 mg/l NH_3
RESIDUAL (mg/l)
TIME (HOURS)
0
10
20
30
40
50

FIGURE 20

Examination of the figures reveals that, in general, bromamine stability may be improved by increasing the ammonia-to-bromine ratio, by increasing the pH, or by decreasing the temperature. For example, at pH 9.0-9.2, where UV absorption shows bromamine present only as NH_2Br: for ammonia and bromine concentrations of 1000 and 50 mg/l respectively, the initial bromamine concentration is reduced to 50% after 11.7 hours contact time; with 10 mg/l of each the bromamine concentration is reduced to 50% of the initial concentration in 0.9 hours; and for ammonia and bromine concentrations of 10 and 50 mg/l, only 50% of the initial bromamine concentration remains after 0.075 hours.

In figures 23 and 24, the bromamine stability at pH 6 appears improved over that at pH 7. This is due to the presence of tribromamine. In both cases the UV spectra at pH 7 was indistinct, and it is assumed that the bromamine was primarily $NHBr_2$. At pH 6, however, UV absorption showed that a major portion of the bromamine was present as NBr_3. It appears that NH_2Br is the most stable bromamine species, and $NHBr_2$ the least stable as is reported by Galal-Gorchev and Morris.[4,5]

F. NOTES ON THE REACTION OF BROMIDE ION WITH CHLORINE

If hypochlorite is added to a solution containing bromide ion, the resulting solution has a free bromine concentration from the formation of hypobromite equivalent to the Br^- concentration of the unchlorinated solution. Addition of Br- to a chloramine solution reduces chloramine stability, apparently due to the formation of bromamine. Ultra violet absorption indicates only chloramine is present. It appears that bromamine is formed in too small a concentration and is too unstable to be detected by ultra violet absorption. However, solutions of mixtures of chloramine and bromide ion exhibit the stability characteristics of bromamine solutions, i.e., their stability depends on ammonia-to-bromine (in this case in the form of bromide ion) ratios and on pH.

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4. H. A. Galal, "Bromoamides; Their Formation and Occurrence in Aqueous Solution", Doctoral Thesis, Radcliffee College, Cambridge, Mass., June, 1961

5. H. Galal-Gorchev, J. C. Morris, "Bromamides in Aqueous Solution", Presented by the Division of Water Waste Chemistry at the Atlantic City Meeting of the American Chemical Society, September, 1962.

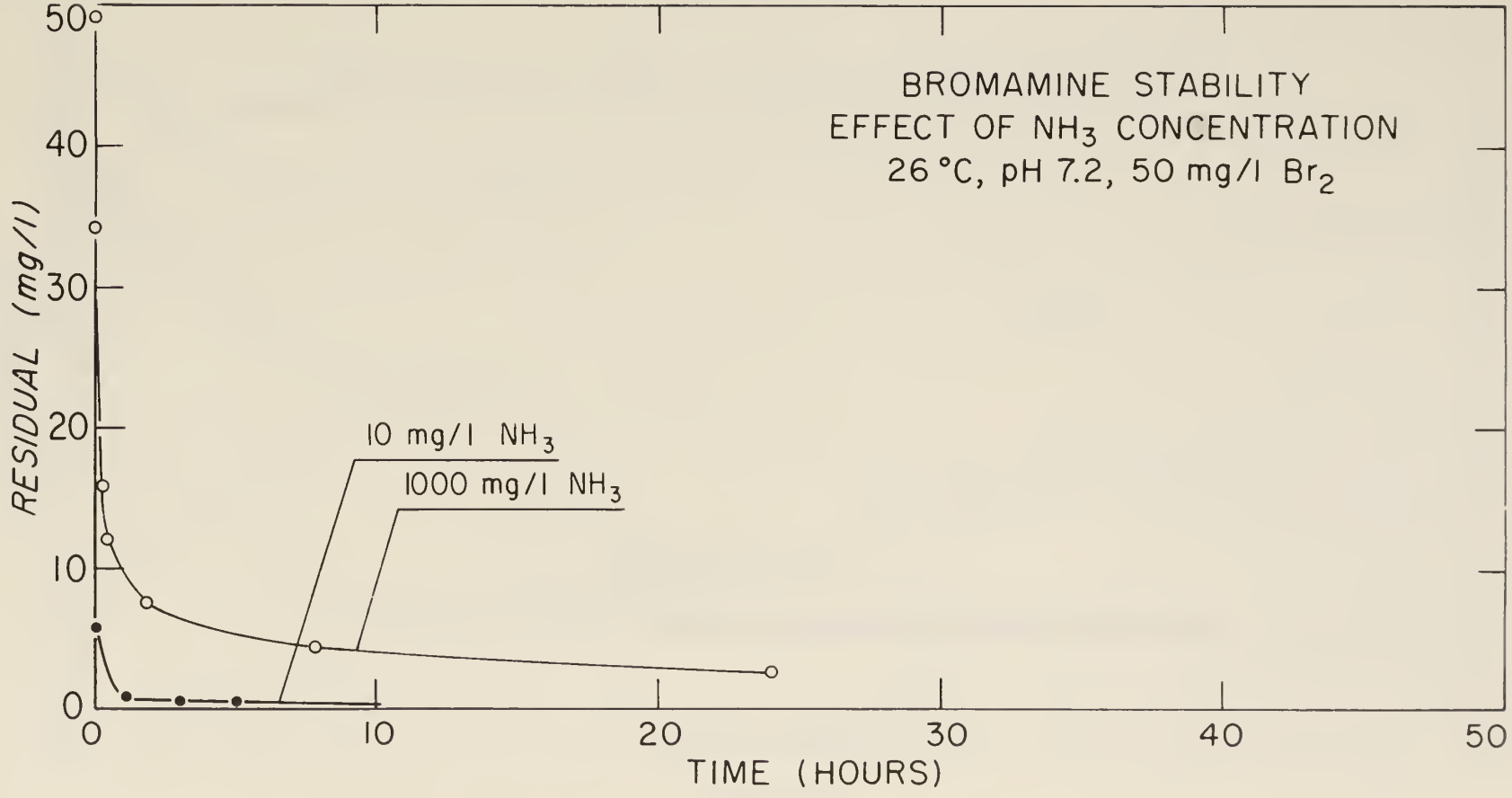
BROMAMINE STABILITY
EFFECT OF NH_3 CONCENTRATION
26 °C, pH 7.2, 50 mg/l Br_2
10 mg/l NH_3
1000 mg/l NH_3
RESIDUAL (mg/l)
TIME (HOURS)
0
10
20
30
40
50

FIGURE 21

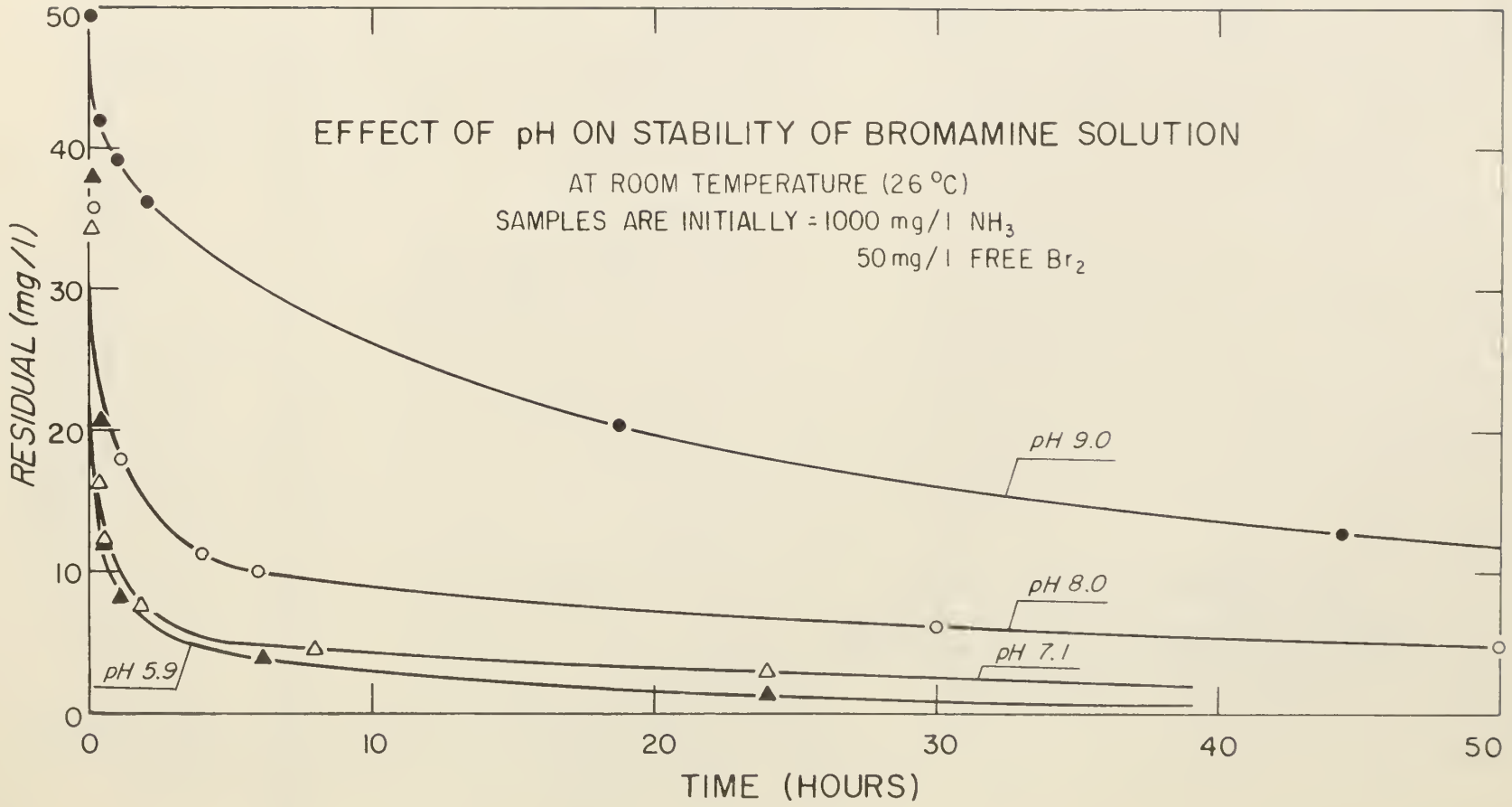
EFFECT OF pH ON STABILITY OF BROMAMINE SOLUTION
AT ROOM TEMPERATURE (26 °C)
SAMPLES ARE INITIALLY = 1000 mg/l NH_3
50 mg/l FREE Br_2
RESIDUAL (mg/l)
TIME (HOURS)
pH 9.0
pH 8.0
pH 7.1
pH 5.9
0
10
20
30
40
50

FIGURE 22

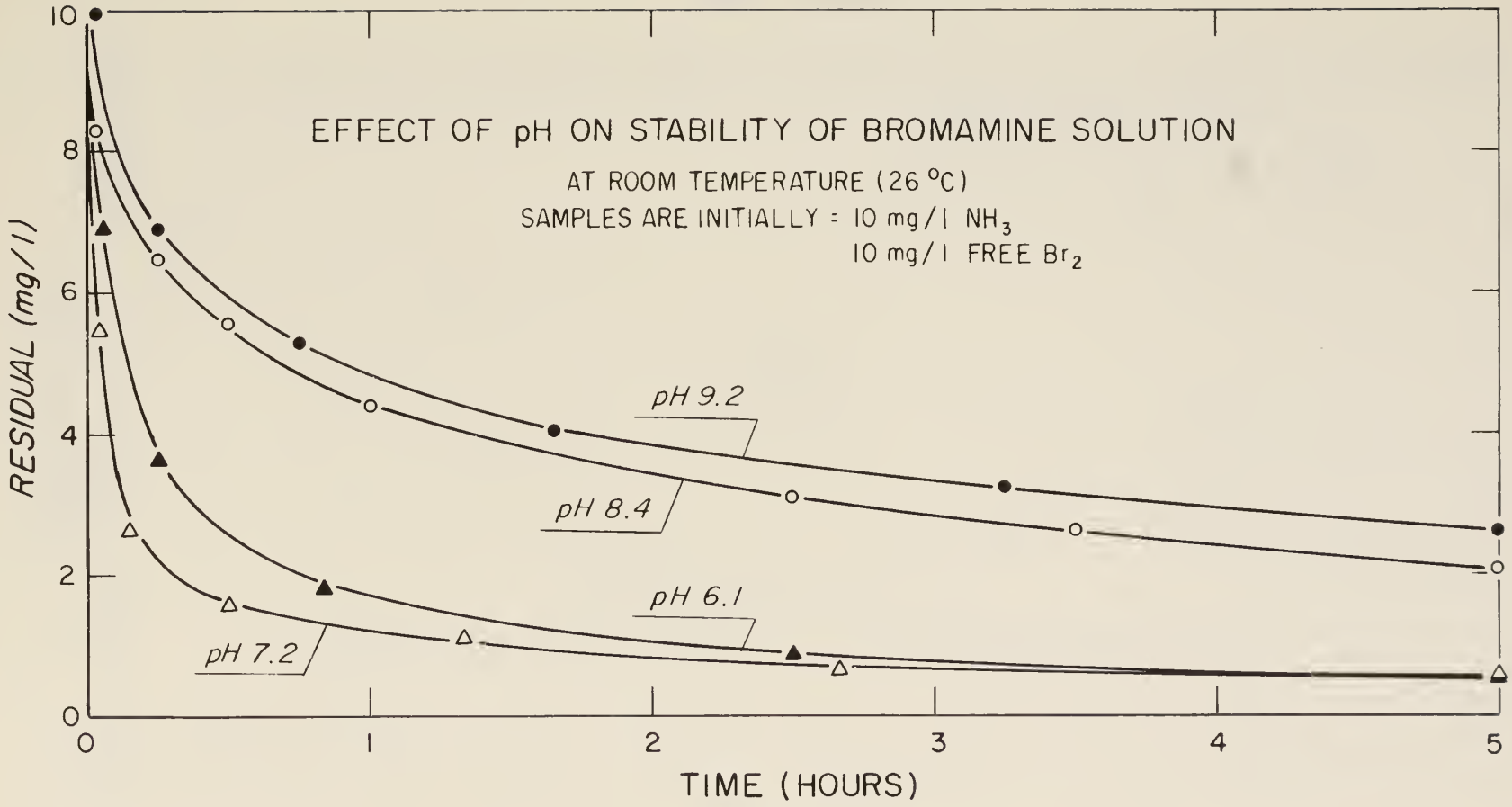
EFFECT OF pH ON STABILITY OF BROMAMINE SOLUTION
AT ROOM TEMPERATURE (26 °C)
SAMPLES ARE INITIALLY = 10 mg/l NH_3
10 mg/l FREE Br_2
pH 9.2
pH 8.4
pH 6.1
pH 7.2
RESIDUAL (mg/l)
TIME (HOURS)
0
2
4
6
8
10
0
1
2
3
4
5

FIGURE 23

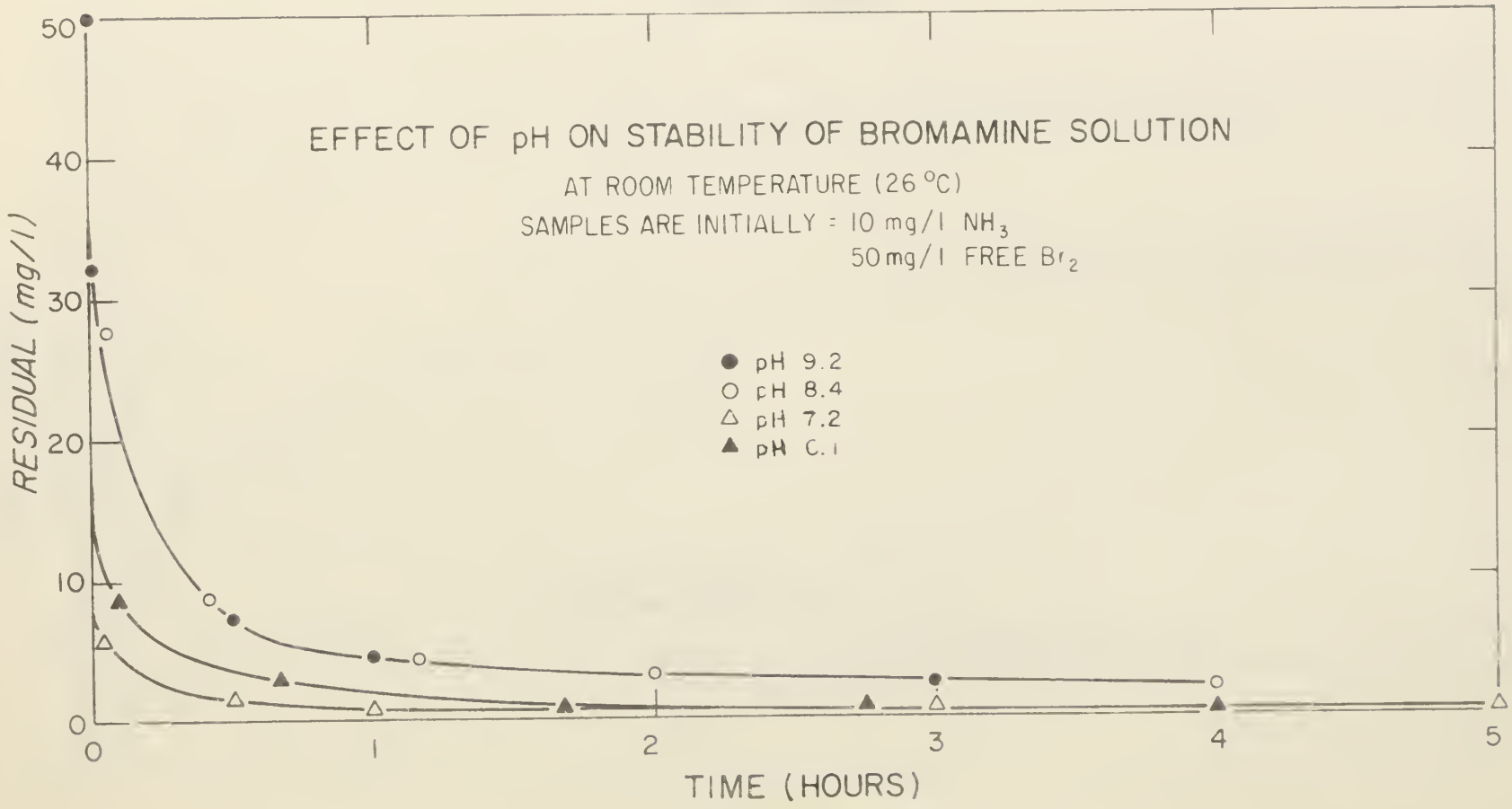
EFFECT OF pH ON STABILITY OF BROMAMINE SOLUTION
AT ROOM TEMPERATURE (26 °C)
SAMPLES ARE INITIALLY = 10 mg/l NH_3
50 mg/l FREE Br_2
● pH 9.2
○ pH 8.4
△ pH 7.2
▲ pH C.1
RESIDUAL (mg/l)
50
40
30
20
10
0
0
1
2
3
4
5
TIME (HOURS)

FIGURE 24

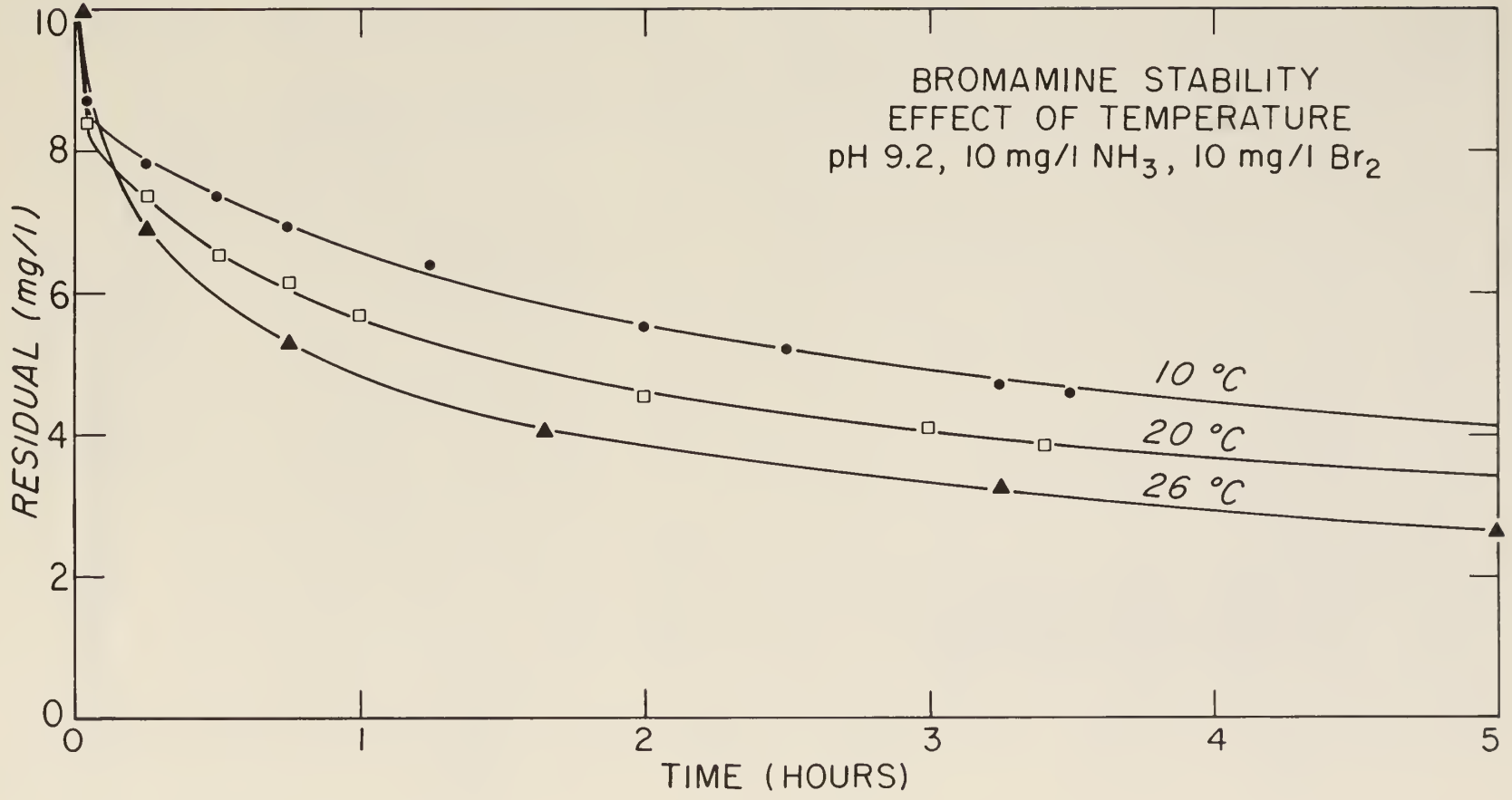
BROMAMINE STABILITY
EFFECT OF TEMPERATURE
pH 9.2, 10 mg/l NH_3, 10 mg/l Br_2
10 °C
20 °C
26 °C
RESIDUAL (mg/l)
TIME (HOURS)
0
2
4
6
8
10
0
1
2
3
4
5

FIGURE 25

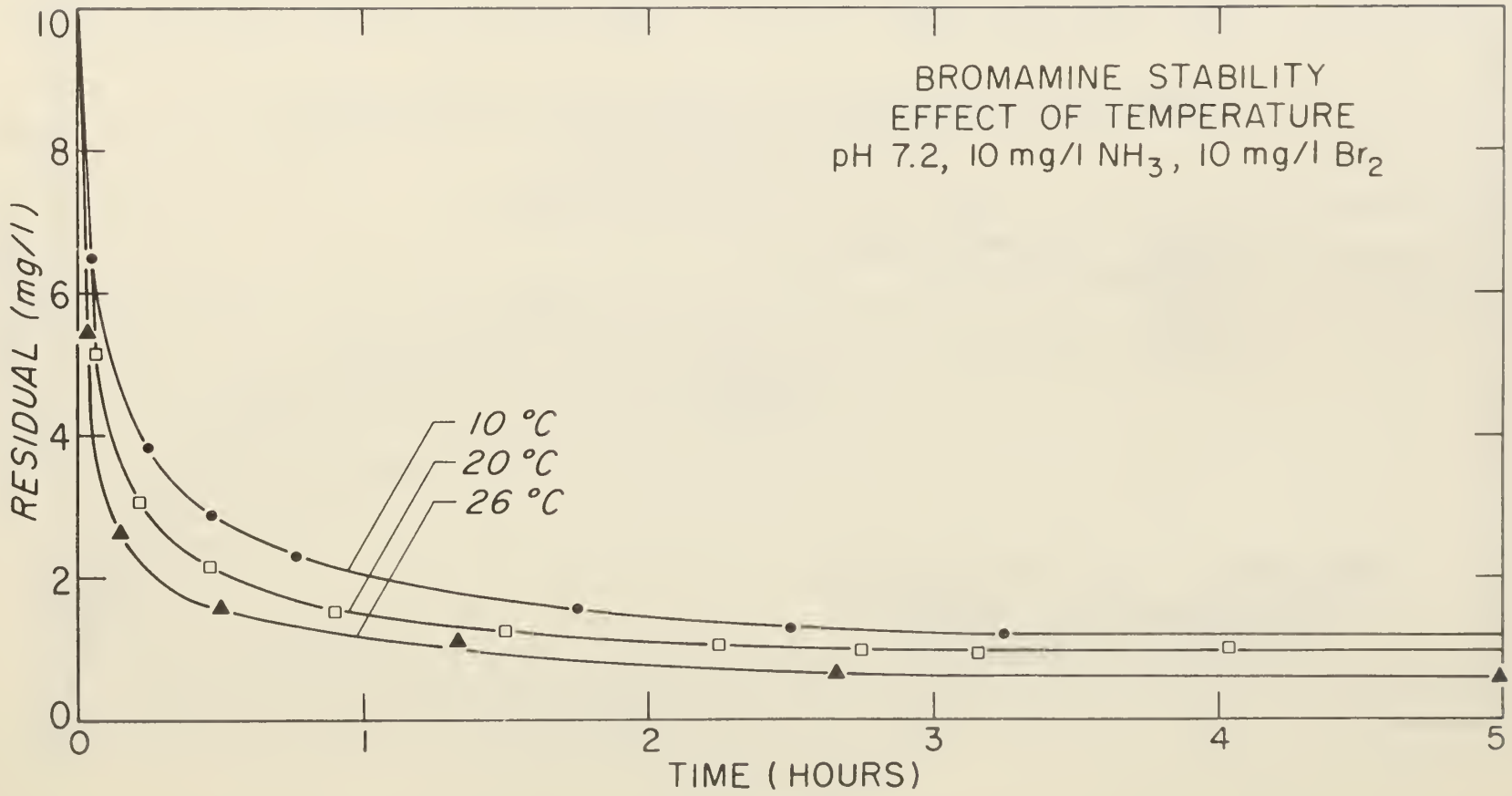
BROMAMINE STABILITY
EFFECT OF TEMPERATURE
pH 7.2, 10 mg/l NH_3, 10 mg/l Br_2
10 °C
20 °C
26 °C
RESIDUAL (mg/l)
TIME (HOURS)
0
2
4
6
8
10
0
1
2
3
4
5

FIGURE 26

G. SUMMARY OF RESULTS

Four colorimetric tests, methyl orange, phenol red, brom cresol purple, and phenosafranin have been found useable to determine bromine, bromamine, chlorine, and chloramine in natural water.

Methyl orange can be used as a quantitative reagent for total residual bromine plus free chlorine. If sufficient bromide ion is added, then total residual bromine and total residual chlorine can be determined. Free bromine calibration curves are nearly linear through the range 0.0-4.0 mg/l at temperatures of 2°, 10°, 20°, 30°, and 40°C and display slight temperature dependence.

Phenol red is used for the determination of total residual bromine in concentrations to 5 mg/l. Free chlorine and chloramine in concentrations to 6 mg/l do not interfere. This would make phenol red a highly desirable bromine test. However, there is one problem which must still be resolved. The non-linearity of the standard calibration curve between 0.0 and 1.0 mg/l free bromine indicates the presence of impurities in the reagent. Three separate batches of phenol red reagent* have been tested; neither has produced a completely linear curve. Thus far no method has been successful for purifying the reagent.

Brom cresol purple reagent is suitable for determining both free bromine and chlorine and is uniquely insensitive to bromamine and chloramine. This test is based on the bleaching effect of bromine on brom cresol purple at pH 9.4. Of all the reagents studied, it comes closest to being specific for free bromine. The standard calibration curve is non-linear below 1 mg/l free bromine. Some temperature dependence may be observed. Free chlorine interferes at a rate equivalent to about 20% of its concentration in 2 minutes.

Phenosafranin is the least sensitive of the four reagents and thus may be of value in determining high bromine concentrations (up to 10 mg/l) at pH 9.2. The standard calibration curve is linear and is not temperature dependent. Chloramine produces no interference on phenosafranin, bromamine interference is slight (about 1.5% of its concentration at 2 minutes), and free chlorine interference is serious (ranging from 14% of its concentration at 2°C to 85% of its concentration at 40°C at 2 minutes).

The other interferences - ferric iron, nitrite, and manganic manganese - have negligible effect on the four reagents discussed above.

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* Merck & Co., No. 53103.
Fisher Certified Reagent A.C.S., P-74.
Matheson Coleman & Bell, NB-160, PX530.

Our work with bromine and its reaction with ammonia verifies some of the extensive work done by J. Carrell Morris and Hend-Galal Gorchev[6]. A solution of monobromamine was prepared at pH 8.8 with a N/Br ratio of 25/1 by weight. At all pH's decreasing the ammonium ion excess decreases the proportion of dibromamine. This species is the least stable of the three amines and always coexists with monobromamine and tribromamine. The best conditions for forming the third species, tribromamine, are a pH of 4.5 - 5.0 and a Br/N ratio of 3/1. We were not able to prepare tribromamine alone, but always found some $NHBr_2$ or OBr- present. Ultra violet absorption gave only qualitative determinations of the bromamines. We have no other means of measuring the individual bromamine species, due primarily to their lack of stability.

Bromamine and chloramine breakpoint data show that bromamines are considerably less stable than chloramines and that in general stability can be improved by increasing the N/Br ratio, increasing the pH, and decreasing the temperature. However, pH does not strictly follow this relationship; below pH6, decreasing the pH promotes tribromamine formation, improving stability.

In the presence of bromide ion, chloramine becomes activated, probably by the formation of bromamine. Although ultra violet absorption shows only chloramine to be present, nevertheless the chloramine-bromide solutions behave as though a small quantity of bromamine were formed. Varying the N/Br ratio or the pH has the same effect on chloramine-bromide solutions as it does on bromamine solutions.

H. CONCLUSIONS

It seems probable that free bromine alone may be determined; and it is possible that free bromine, free chlorine, bromamine, and chloramine may be distinguished from one another.

Methyl orange serves well to indicate bromine, bromamine, chlorine, and chloramine (in the presence of bromide ion). The primary weakness of the test is that it relies on a bleaching reaction which necessitates accurate measurement of the quantity of reagent used.

Phenol red is a unique test for total bromine, including bromamine, with no interference from free chlorine and chloramine. The greatest difficulty encountered with phenol red appears to be due to reagent impurity. The calibration curve is linear above 1 mg/l free bromine, but for lower bromine concentrations exhibits a decided bend, which is believed to result from the impurity of the reagent. Thus far no method has been successful for purifying the reagent.

6. H. Galal-Gorchev, J. C. Morris, (see footnotes 4 & 5 of this report).

The brom cresol purple reaction is based on the bleaching effect of bromine on the reagent at pH 9.4. Of the reagents studied, brom cresol purple is closest to being specific for free bromine. The reagent is uniquely insensitive to bromamines and chloramines, but is suitable for the determination of free bromine and free chlorine. There remains an unexplained problem of slight temperature dependence; the bromine calibration curve slope increases with decreasing temperature.

Phenosafranin reagent is bleached by bromine at pH 9.2. The reagent is insensitive to chloramine. Bromamine causes negligible interference if absorbance is determined in two minutes. Free chlorine produces a serious interference. Phenosafranin may be primarily useful in measuring high concentrations of free bromine (up to 10 mg/l).

Breakpoint curves for both chlorine and bromine indicate more rapid reaction of bromine than chlorine, especially at high pH, and emphasize the lack of stability of bromamine as compared with chloramine.

Further work will be needed on the temperature dependence of brom cresol purple and phenol red tests and on improving the linearity of their calibration curves. Further work will be needed, too, on the stability of the 4 reagent solutions over an extended time. Finally, the four selected tests must be thoroughly evaluated in polluted waters.

VI. APPENDIX

EXPERIMENTAL METHODS

All solutions were prepared using double distilled, ammonia free water unless otherwise specified. A Sargent water bath and cooler was used in controlled temperature studies. Absorbance readings were made with a Beckman Model DB spectrophotometer with a 1.0 cm cell at the wave length of maximum abosrbance for the reagent being tested.

Stock solutions were prepared as follows:

1. Bromine stock solution: One ml liquid bromine was added to 15 ml 20% NaOH and about 450 ml water. The solution was mixed to dissolve the bromine and then diluted to 500 ml and stored in a glass stoppered bottle away from light. A new solution was prepared every two weeks. The bromine solution contained about 5% bromate initially and little change in bromate concentration was observed during a two week time period. Each morning a standard free bromine solution was prepared by dilution of the stock bromine solution and standardized by iodometric titration against sodium thiosulfate. (The sodium thiosulfate solution was standardized every 7 days against potassium dichromate). Procedure for the standardization may be found in the section "Procedures for the Standardization of Free Bromine Solutions."

2. Bromamine stock solutions:

   a. Monobromamine: 13.6 ml 0.1% $(NH_4)_2SO_4$, 5 ml 0.042 M borax, 0.7 ml 20% NaOH and sufficient bromine to make the final solution 3 mg/l were added in the order listed to 100 ml water while mixing on a magnetic stirrer. The resulting solution was diluted to 200 ml and had a N/Br ratio of 20/1 by weight and a pH of 8.8. It was assumed to be entirely monobromamine (NH_2Br).

b. Dibromamine: Dibromamine solution was prepared by adding, in the order listed, 0.68 ml 0.1% $(NH_4)_2SO_4$, 5 ml phosphate buffer pH 6.9 (35 g Na_2HPO_4, 17 g KH_2PO_4, and 20 mg $HgCl_2$ per liter), and sufficient bromine for a final concentration of 3 mg/l to 100 ml water while mixing on a magnetic stirrer. The resulting solution was diluted to 200 ml and had a N/Br ratio of approximately 1/1 by weight and a pH of 7.3. It is a mixture of NH_2Br and $NHBr_2$ as may be seen by UV absorption. Dibromamine solution cannot be prepared free of both NH_2Br and NBr_3.

c. Tribromamine: Tribromamine solution was prepared by adding, in the order listed, 5.3 ml 0.001% $(NH_4)_2SO_4$, 5 ml buffer pH 5.06 (150 ml 0.5 M $NaC_2H_3O_2$ and 100 ml 0.5 M CH_3COOH), and sufficient bromine for a final concentration of 1.5 mg/l to 100 ml water while mixing on a magnetic stirrer. The final solution was diluted to 200 ml and had a N/Br ratio of approximately 0.15/1 by weight and a pH of 5.18. Ultra violet absorption indicated that the solution contains both NBr_3 and a small quantity of OBr-.

Bromamine solutions were prepared as indicated above to check bromamine interference with the proposed reagents. Solutions of greater bromamine concentrations may be prepared by increasing the $(NH_4)_2SO_4$ and NaOBr concentrations while maintaining the same weight ratio.

Since the bromamine solutions are very unstable, at the time each bromamine sample was tested an identical sample was tested with methyl orange. Results of the methyl orange test were used as a measure of the total bromamine present at that time.

3. Chlorine stock solution: A standard free chlorine solution was prepared each morning by dilution of Clorox (5.25% NaOCl) and standardized iodometrically against sodium thiosulfate.

4. Chloramine stock solution: The solution was prepared from 0.1092 mg/l ammonium chloride and 1 ml clorox with 168 mg/l sodium bicarbonate to adjust pH to 7.8-8.2. The solution was allowed to stand for at least 12 hours (overnight), then standardized immediately before use by the methyl

orange test. Such a solution is exclusively monochloramine. The N/Cl ratio is approximately 1/1 by weight.

5. Nitrite solution: Nitrite solution was prepared using sufficient $NaNO_2$ to yield 500 mg/l nitrite ion.

6. Manganic ion solution: A stock solution of $MnSO_4.H_2O$ was prepared and standardized colorimetrically. Prior to use (maximum time, 1 hour), the pH was adjusted to 10 with NaOH and, after 10 minutes, neutralized with H_2SO_4. The maximum concentration of manganese which could be oxidized without precipitation was 6.7 mg/l.

7. Ferric iron solution: A stock solution of $FeCl_3.6H_2O$, with 168 mg/l $NaHCO_3$ added, was prepared and standardized.

Procedure for the Standardization of Free Bromine Solution:

The following procedure has been adopted for standardization of free bromine solutions.

To determine free bromine (OBr-), a 200 ml sample is added to about 3 g KI crystals and mixed gently. Then 1 ml glacial acetic acid is added to reduce the pH to 4.0 and the solution is titrated iodometrically against 0.025 N $Na_2S_2O_3$ to a starch endpoint. (The $Na_2S_2O_3$ has been previously standardized against $K_2Cr_2O_7$). To determine total bromine (OBr-, OBrO-, $OBrO_2^-$), 2 ml 20% Br- solution and 8.3 ml concentrated HCl are substituted for the glacial acetic acid, and the resulting solution has a pH of 0.5. It is titrated iodometrically just as for free bromine.

Standardization of Bromamine Solutions:

The methyl orange test provides a quantitative determination of bromamine, but does not distinguish between the 3 forms. UV absorption may be used to determine which species are present (i.e., a maximum at 280 mμ, indicates NH_2Br; at 230 mμ, $NHBr_2$; and at 260 and 330 mμ, NBr_3). At the present time no procedure is available for the quantitative determination of a single species.

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5. AUTHOR(S) *(First name, middle initial, last name)*: T. E. Larson and F. W. Sollo, Jr.

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11. SUPPLEMENTARY NOTES	12. SPONSORING MILITARY ACTIVITY
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13. ABSTRACT

Twenty-seven colorimetric reagents were evaluated on the basis of their reactions with bromine, chlorine, chloramines and bromamines. At the present time methyl orange and phenol red are the best available reagents for total bromine, and are in good agreement. Brom cresol purple is the best available reagent for free bromine. Phenosafranin gives reasonably good results for free bromine, but its primary application may be in determining high concentrations of bromine (up to 10 mg/l).

Breakpoint curves with bromine and ammonia have been determined for varied contact times and at different pH values.

The bromamines are far less stable than the chloramines. Studies of the stability under varying ammonia-to-bromine ratios and varying pH values have been made.

A study was made of the reaction of chloramines with bromide ion. No evidence of bromamine formation was found by ultra-violet absorption, but stability of the chloramine solution was decreased, and it appears that unstable bromamine was formed slowly. The chloramine-bromide ion solutions exhibited characteristics similar to those of bromamine solutions. As with bromamine solutions, the stability of chloramine-bromide solutions may be improved by increasing the ammonia-bromine (or bromide ion) ratio or by increasing pH.

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Security Classification

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
	Not	REQUIRED			—	
Analysis						
Water						
Bromine						
Methyl Orange						
Phenol Red						
Brom Cresol purple						
Phenosafranin						